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THE HOMOGENEOUS REDUCTION OF ALKYNES
BY CHROMIUM (II)

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
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ABSTRACT

The homogeneous reduction of alkynes by chromium (II) ion has been studied. The reaction was found to follow the rate equation

$$v = k_3(\text{Cr}^{\text{II}})^2(\text{Alkyne})(\text{H}_3\text{O}^+)^{-1.3}$$

in solutions of constant ionic strength. The reduction of phenylpropionic acid, N,N,N-trimethyl-(para-ethynylphenyl) ammonium chloride, N,N,N-trimethyl-4-phenyl-3-butynyl ammonium chloride, and N,N,N-trimethyl-3-phenyl-2-propynyl ammonium chloride have been investigated, and in all cases except that of the last named compound, the products under conditions of kinetic control were the trans-ethylene and the mononuclear hexaquo chromium (III) ion. The propynyl ammonium chloride on the other hand, yielded mainly the cis-ethylene and a dinuclear chromium (III) ion. The reduction of phenylpropionic acid was found to have a ΔH^\ddagger of 4.94 kcal/mole. and a value for ΔS^\ddagger of -42.6 eu/mole., and these values lead to a value for ΔF^\ddagger at 40°C of 18.3 kcal/mole.

The reduction of phenylpropionic acid was shown by an examination of the plot of $\log k_{\text{obs}}$ versus pH, to proceed almost entirely via the undissociated acid, which was found to be reduced approximately 10^4 times as fast as the acid anion.

The reduction of phenylpropionic acid showed a deuterium isotope effect of 7.5, which consisted of a contribution from the acid rate depression term in the rate expression, and a term to account for the change in location of the hydration sphere during the oxidation of chromium (II) to chromium (III), together with the contribution from O-H bond cleavage in the rate determining step. After correcting

for the first two terms, the contribution from O-H bond cleavage was found to be between 1.7 and 2.5. This value is consistent with a hydride ion transfer in the rate determining step. The Hammett ρ value for the reaction was found to be +0.3, which is also consistent with the transfer of a negative entity to the organic substrate in the rate determining step. Three mechanisms are given which are compatible with these experimental observations.

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HISTORICAL

(i) A BRIEF SURVEY OF REDOX REACTIONS

The terms oxidation and reduction appear to have been introduced in the middle years of the nineteenth century as terms descriptive of reactions in which materials either gained or lost oxygen. These definitions were later extended to include loss or gain of hydrogen, and in the early years of this century, with the introduction of the electronic concept of valence, all reactions in which materials either lost or gained electrons came to be classified as oxidations or reductions. The concept of electron transfer has dominated thought concerning redox reactions since its introduction, and as recently as 1955 it was possible for the following statement to appear in the literature without causing a great deal of adverse comment: "The true mechanism of organic oxidation may well be identical with the well recognised definition of oxidation, i.e. a loss of electrons." (1). However, while it is probably true that a large number of redox reactions proceed by electron transfer mechanisms, an increasingly large number of reactions are known in which atom or group transfer is a necessary part of the reaction mechanism. Hence it is possible to distinguish between two extreme types of redox reaction: Those in which the mechanistically significant step is the transfer of electrons, and those in which atoms or groups are transferred in the rate determining stage. Clearly it is not possible to divide sharply all redox reactions into two such rigidly defined classes, and as has been emphasised elsewhere, (2) it is possible that a complete spectrum of reaction mechanisms exists between these two extremes. For example, the reaction between the

argonium ion Ar^+ and the argon atom in the gas phase must certainly proceed by electron transfer.



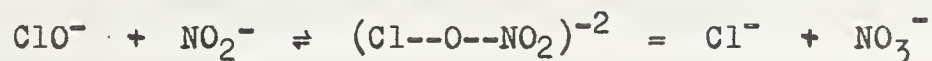
However, such clear cut examples are rare, and even in the case of the reaction between ferro- and ferricyanide,



where there is no evidence for group transfer, Stewart (2) has pointed out that since in aqueous solution the ferrocyanide will be more highly solvated than the ferricyanide ion, when electron transfer takes place, and the positions are reversed, there is no doubt that some water molecules in the outer coordination sphere of the original ferrocyanide ion will be transferred to the newly formed ferrocyanide ion. At the other end of the scale one may consider the oxidation of the nitrite ion by hypochlorite.



This reaction has recently been investigated by Anbar and Taube (3), who have demonstrated by the use of O^{18}Cl^- that the labeled oxygen atom from the hypochlorite ion is essentially completely transferred to the nitrite ion during the reaction.



Hence the mechanistically significant step in this reaction is the transfer of an oxygen atom, i.e. atom transfer.

A series of reactions which appear to have mechanisms

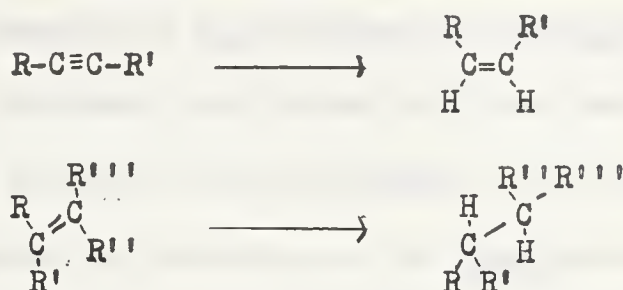
lying between these two extremes is that recently studied by Taube and coworkers (4,5) between $\text{Cr}(\text{H}_2\text{O})_6^{+2}$ and $\text{Co}(\text{NH}_3)_5\text{X}^{+2}$, where X is CNS^- , N_3^- , AcO^- , Br^- , Cl^- , oxalate, phosphate and sulphate. In each case the group X is transferred to chromium during the reaction:



However, it is by no means clear that the mechanistically significant step in these reactions is the cleavage and formation of strong bonds to X, i.e group transfer, and it is possible that the rate determining step is the transfer of an electron from chromium to cobalt, the group X acting simply as a convenient bridge, in the first instance reducing the coulombic repulsion between the two ions and thus reducing the energy of approach, and secondly by providing a low energy path for the flow of electrons. Taube (4b) has presented evidence that in the case of the reduction of IrCl_6^{-2} by $\text{Cr}(\text{H}_2\text{O})_6^{+2}$, there is no transfer of chlorine, since in this case, of the possible products, IrCl_6^{-3} and $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{+2}$, the iridium complex is the more stable. This observation suggests that in the cobalt reactions, the transfer of the group X may not be rate determining, and may take place simply because $\text{Co}(\text{NH}_3)_5\text{X}^+$ is less stable than $\text{Cr}(\text{H}_2\text{O})_5\text{X}^{+2}$, and hence when the reaction intermediate splits, X remains attached to the chromium rather than to the cobalt ion. These considerations make it clear that in any investigation into the mechanism of a redox reaction, the distinction between electron transfer and atom transfer must be clearly born in mind, although in many instances it may require very sophisticated experimentation to distinguish between the two.

(ii) THE REDUCTION OF CARBON-CARBON MULTIPLE BONDS

There are three general methods for the reduction of carbon-carbon multiple bonds. These are: 1) catalytic hydrogenation; 2) reduction at a metal surface during the dissolution of the metal in either acidic or alkaline media; and 3) the use of a metal, generally an alkali metal, dissolved in a solvent such as liquid ammonia or an alcohol, which contains a labile hydrogen atom. Of these, the first almost invariably gives rise to products resulting from cis-addition to the bond. For example, acetylenes yield cis-ethylenes, and ethylenes give rise to erythro- or meso-compounds.

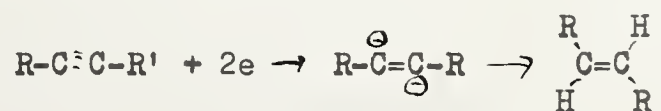


Various workers (6,7,8,9) have reported that zinc in acetic acid gives trans-addition to the triple bond. Ott and coworkers (10) have investigated the reduction of double and triple bonds using aqueous solutions of ammonium hydroxide and ammonium chloride as solvent and a metal as catalyst, and have shown that the stereochemical course of the reaction depends on the nobility of the metal used. They reported that the more noble metals yield exclusively cis-addition, while baser metals yield mixtures of cis- and trans- isomers. The very basic metals such as sodium and calcium gave no ethylenic compound when used to reduce acetylenes, but yielded a 50:50 mixture of the fully saturated compound and unchanged acetylene. However, Ott did not discuss the possibility of mechanistic differences between different metals, and did not examine the possibility that his results were caused by

differing amounts of isomerisation occurring during the work up or during the reaction. It seems hardly likely that all reductions of multiple bonds proceed by similar mechanisms, and it is doubtful if any meaningful conclusion can be drawn from this work.

Rabinowitch and Looney (11) have briefly re-examined some of the earlier reported trans-reduction of some acetylenes, and they report that contrary to the results of Aronstein and Holleman (6), diphenylacetylene, on reduction with zinc and acetic acid, yields cis-stilbene. They also reported that the reduction of acetylene-d₂ and propyne-d₁ using zinc and acetic or zinc and hydrochloric acid leadsto the formation of cis-ethylene-d₂ and cis-propene-d₁ respectively. However, they showed that the reduction of these two compounds with sodium in liquid ammonia, or with chromium (II) chloride in hydrochloric acid gave the trans-reduction products. More recently, Clarke and Crombie (12) have shown that the reduction of several acetylenic compounds with zinc and hydrochloric acid always gave the cis-addition products. These observations suggest that in the earlier work it is possible that cis-trans-isomerisation occurred during the reaction or the work up of the products. It remains to be seen whether this is so or not, and it seems desirable that much of this work should be repeated.

The use of sodium in liquid ammonia generally gives rise to trans-reduction of acetylenes. Greenlee and Fernelius (13) have proposed the following mechanism.



In the intermediate dianion, it was postulated that the electrostatic repulsion between the electrons in the two fully occupied

p-orbitals was sufficiently great to maintain the molecule in the trans-configuration during the subsequent proton abstractions from the solvent. However, this mechanism seems rather unlikely, for in the first place it seems improbable that the dianion would be formed at all, since the transfer of one electron to the acetylene molecule would no doubt be followed by a rapid proton abstraction from the solvent before the second electron could be transferred. Secondly, even if the dianion were formed, the introduction of one proton would destroy the electrostatic repulsion, and lead to possible equilibration between the cis- and trans- forms of the monoanion. It would therefore appear that further investigation into the mechanism of this reaction would be profitable.

(iii) SOME REACTIONS OF CHROMIUM (II)

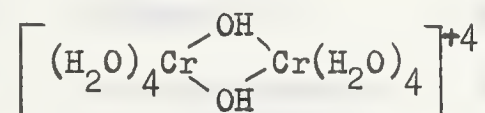
Chromium (II) is a well known inorganic reducing agent, and has been used as either a one or two equivalent reducing agent. The work of Taube in connection with the one equivalent reductions has already been mentioned. He has shown that where there is the possibility of bridging between the oxidant and the reductant chromium ion, via a ligand which can form coordinate bonds to both ions, reactions proceed very much more rapidly than when there is no such bridging. For example, Anderson and Bonner (14) have shown by the use of radioactive chromium, that at 25° in 1.00 N. perchloric acid, the rate of the reaction



is very slow ($k \approx 10^{-5}$). However, when a chlorine atom is present in the coordination sphere of the chromium (III) ion, the rate is increased by a factor of about 10^6 (15), due to the formation of a chloride bridge between the reacting ions, which provides a path of lower energy for the electron flow. This effect is shown in a still more impressive manner when a comparison is made between the reduction of $\text{Co}(\text{NH}_3)_5(\text{succinnate})^+$ and $\text{Co}(\text{NH}_3)_5(\text{fumarate})^+$ by chromium (II). In these cases, there is the same electrostatic interaction between the two reacting ions in both reactions, and the bonds to chromium and cobalt are the same for both intermediates. However, the fumarate complex is reduced several hundred times faster than the succinnate complex (5). This has been explained on the basis of the unsaturated ligand providing a lower energy path for the transfer of electrons than does the saturated one. This result

when coupled with the observation that there is no atom transfer in the reduction of IrCl_6^{-2} carries a strong implication that in reactions where bridging is important, atom transfer may not be a significant part of the reaction mechanism, which may proceed by electron transfer in all cases, and atom transfer occurs only when the relative stabilities of the possible products require that the atom be transferred.

The reactions of chromium (II) as a two equivalent reducing agent have been less extensively studied. Ardon and Plane (16) have shown that when chromium (II) salts act in this fashion, the chromium (III) species which is produced is not the purple $\text{Cr}(\text{H}_2\text{O})_6^{+3}$ ion which is formed in one electron transfer reactions, but a green dinuclear species, which they tentatively identify as



The formation of this species in the reactions of chromium (II) salts with e.g. O_2 , Tl^{+3} , ClO_3^- , and HClO is explained by a two equivalent oxidation of Cr^{II} to yield a Cr^{IV} species, which reacts with a further Cr^{II} ion to yield the dinuclear ion above.

Although chromium (II) has been used to reduce a variety of organic compounds, (See Table I), both from the preparative and the analytical standpoint, very few mechanistic investigations appear to have been carried out. It is interesting to note that chromium (II) does not appear to reduce alkenes, and as may be seen from Table I, alkenes appear as stable products in several of the reactions of chromium (II) with organic compounds. In the present investigation, an attempt was made to reduce cinnamic acid with chromium (II) perchlorate, but only unchanged starting material was recovered.

TABLE I

SOME APPLICATIONS OF THE CHROMIUM (II) ION IN THE
REDUCTION OF ORGANIC COMPOUNDS

Substance	Product	Use	Reference
ArNO_2	ArNH_2	Preparative	17
ArNO	ArNH_2	Preparative	17
ArN=NAr	ArNH_2	Preparative	17
Anthraquinones	Anthrahydroquinones	Analytical	17
Alkynes	Alkenes	Analytical	17
α -Epoxyketones	α - β -Unsaturated ketones	Preparative	18
1-2-Dibromides	Alkenes	Preparative	19
Benzaldehyde	Hydrobenzoin	Preparative	20
ArC(Cl):NR	ArCHO	Preparative	21

(iv) DEUTERIUM ISOTOPE EFFECTS IN INORGANIC REDOX REACTIONS

In inorganic aquo-ions, the distance between the oxygen atoms of the hydration sphere and the transition metal cation does not have a constant value, but varies with the charge and size of the metal ion. For the same metal, the hydration sphere will be located at different distances from the central ion in different oxidation states. One consequence of this is that when a metal cation changes its oxidation number, the hydration sphere will expand or contract, according to whether reduction or oxidation has occurred. Hence for an inorganic redox reaction, a certain part of the activation energy requirement arises from the change of location of the solvation sphere. This energy requirement would be expected to result in a decrease in the reaction rate when the solvent is changed from H_2O to D_2O . This effect has been observed by Taube et al (22,23,24) in the reduction of $\text{Cr}(\text{NH}_3)_5\text{Cl}^{+2}$ by $\text{Cr}(\text{D}_2\text{O})_6^{+2}$ and $\text{Co}(\text{NH}_3)_5(\text{OH})^{+2}$ by $\text{Cr}(\text{D}_2\text{O})_6^{+2}$. The former reaction had been previously shown to proceed via a transition state in which the chlorine atom was involved in the coordination sphere of both metal ions, and hence no O-H bond rupture would be expected in the transition state. However, after correcting for the difference in acidity between H_3O^+ and D_3O^+ , there was found to be a 30% decrease in the rate in D_2O as compared with H_2O as solvent; i.e. $k_{\text{H}}/k_{\text{D}} = 1.5$, and this is very probably due to the effect discussed above. Taube has also shown (23) that when the bridging group contains hydrogen, as it does in the reduction of the cobalt salt above, the observed isotope effect is of the order of 3.5 to 4. This observation has been interpreted as showing that in these cases, some O-H bond

distortion does take place in the group being transferred. However, when the bridging group contains no hydrogen in the vicinity of the reaction sight, the expected isotope effect is quite small, although not negligible.

The purpose of the present investigation is to elucidate the mechanism of the chromium (II) ion reduction of carbon-carbon triple bonds, and it is hoped that the results described in this thesis will help to shed some light on the mechanisms of the homogeneous reduction of organic compounds, and that we may gain some insight into the field of oxidation and reduction by electron or group transfer.

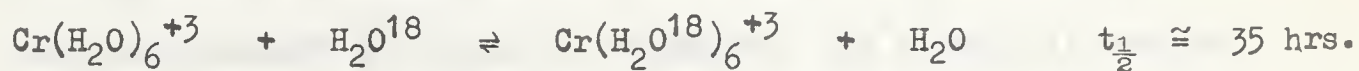
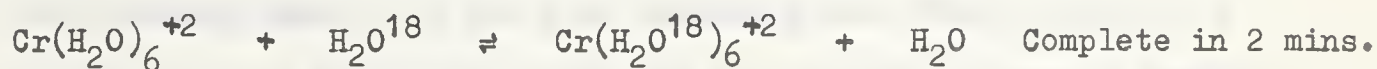
RESULTS AND DISCUSSION

(i) INTRODUCTION

There is little known about the mechanisms of reduction processes of organic compounds by inorganic salts, although a considerable amount of information is available concerning inorganic oxidation reduction reactions, and organic oxidations by both permanganate and chromic acid have received considerable attention (25). For the present study the chromium (II) ion was chosen as the reducing agent. The reasons for this choice were that this reagent has been used in several preparative and analytical procedures (Table I), and that the inorganic chemistry of chromium has been fairly well established. Consequently, it was not necessary to spend a lot of time studying the nature of the various chromium ions which have been encountered in this investigation. Furthermore, the reduction of alkynes by chromium (II) offers an extremely interesting system for study, in that the reaction is stereospecific, yielding a trans-alkene, which is not further affected by the reducing agent. Hence the reaction is of considerable significance preparatively, as well as being interesting from the mechanistic point of view.

(ii) THE SELECTION OF THE MATERIALS

Chromium is a member of the transition group of metals, and in aqueous solutions its salts exist as a variety of relatively stable coordination complex ions. In any solution of a chromium (III) salt it is possible that there may exist one or more different complex ions, and the relative concentrations of these species can change depending on the changing nature of the solution; for example, a change in pH, or in the concentration of an added salt. The situation in solutions of chromium (II) salts is similar, but is further complicated by the fact that chromium (II) salts are very much more labile to ligand substitution than are the salts of chromium (III). For example, Taube and coworkers (26) have shown by the use of O^{18} that the exchange of water between the hydration sphere and the solvent is complete for the hexaquo chromium (II) ion within two minutes, while for the hexaquo chromium (III) ion under the same conditions, the half life of the exchange is about 35 hours.



In view of this, it was necessary to choose a chromium (II) salt in which the anion had very little tendency to enter the inner coordination sphere, and to exclude as far as possible other anions, except in controlled amounts. The most conveniently prepared salt of this nature was chromium (II) perchlorate. The procedure which is described in the experimental section yielded a solution of chromium (II) perchlorate which gave no precipitate with silver perchlorate solution, provided the chromium (II) acetate precipitate

was washed carefully at least four times with distilled water. The solution was shown to contain less than 1% chromium (III), and gave a negative test for zinc. Hence it was possible to ensure that at the start of the reaction all the chromium (II) in the solution was present as the hexaquo ion, $\text{Cr}(\text{H}_2\text{O})_6^{+2}$, and that any foreign ion which might interfere with the kinetics had been rigidly excluded. It is significant that when maximum precautions had been taken to exclude chloride and zinc ion from the stock solution of chromium (II) perchlorate, rate coefficients were a minimum, and were reproducible from batch to batch (Table II). As a result of the observations shown in Table II, a standard procedure of five washings was adopted for all subsequent preparations of chromium (II) perchlorate.

The choice of the organic substrate was governed by several factors. It was necessary for the substance to be water soluble, since the use of aqueous solutions was dictated by the nature of the reducing agent. It was also desirable that there should be a phenyl group in conjugation with the triple bond, so that a Hammett reaction constant (ρ) could be evaluated; and finally it was felt that a solid compound would be more easily purified and handled than a liquid. Phenylpropionic acid presented itself as a compound which fulfilled these requirements, and in addition, it and its para-substituted derivatives are readily prepared by standard methods. However, there are two disadvantages to the use of phenylpropionic acids. In the first place they are relatively strong acids (Table III) and hence their dissociation introduces another variable. This complication may be corrected for, and the calculations are

TABLE II

THE REDUCTION OF PHENYLPROPIOLIC ACID BY CHROMIUM (II) PERCHLORATE
 IN THE PRESENCE OF ACETIC ACID AND SODIUM ACETATE: THE EFFECT OF
 THOROUGH WASHING AND REMOVAL OF FOREIGN IONS ON THE
 RATE OF REDUCTION

Temperature = $40.0 \pm 0.05^\circ$

Ionic Strength = 0.50

(AcOH) = 1.6 mole.l^{-1}

pH = 1.40

Number of Washings	k_3
1	1.21
1	1.33
4	1.03
8	1.04
15	1.02

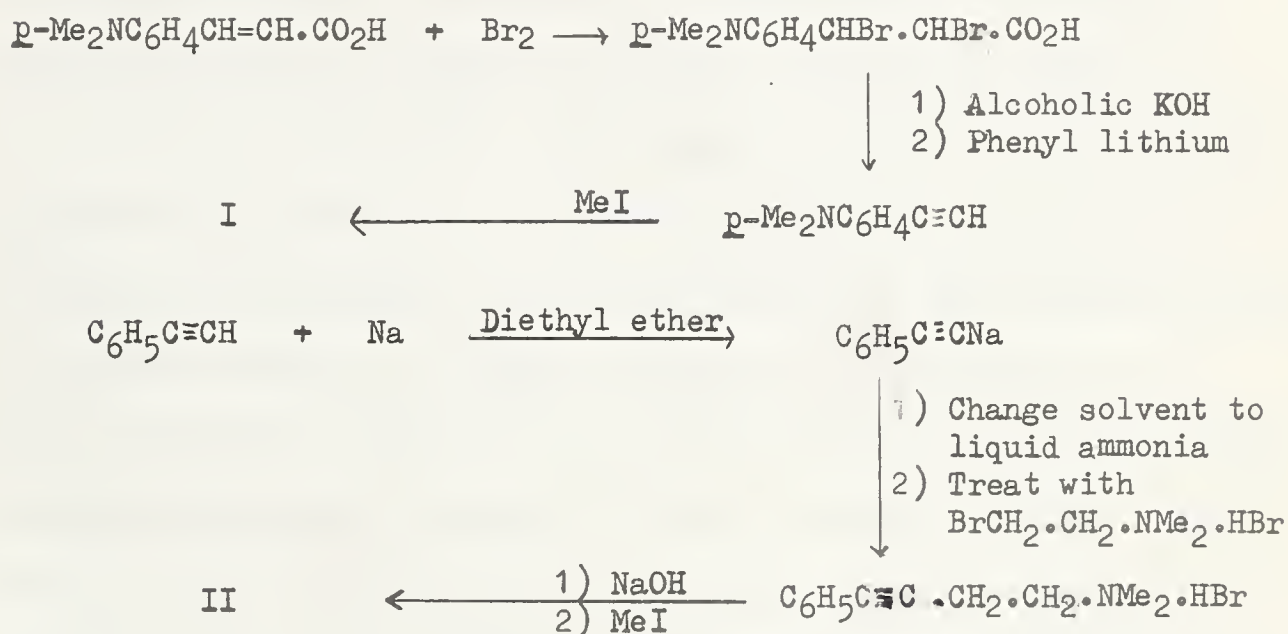
TABLE III

DISSOCIATION CONSTANTS OF para-SUBSTITUTED PHENYLPROPIOLIC
ACIDS AT 25° IN WATER - 25% DIOXANE (27)

Substituent	pK _a
<u>para</u> -Cl-	3.07
<u>para</u> -OMe-	3.44
<u>para</u> -H-	3.24

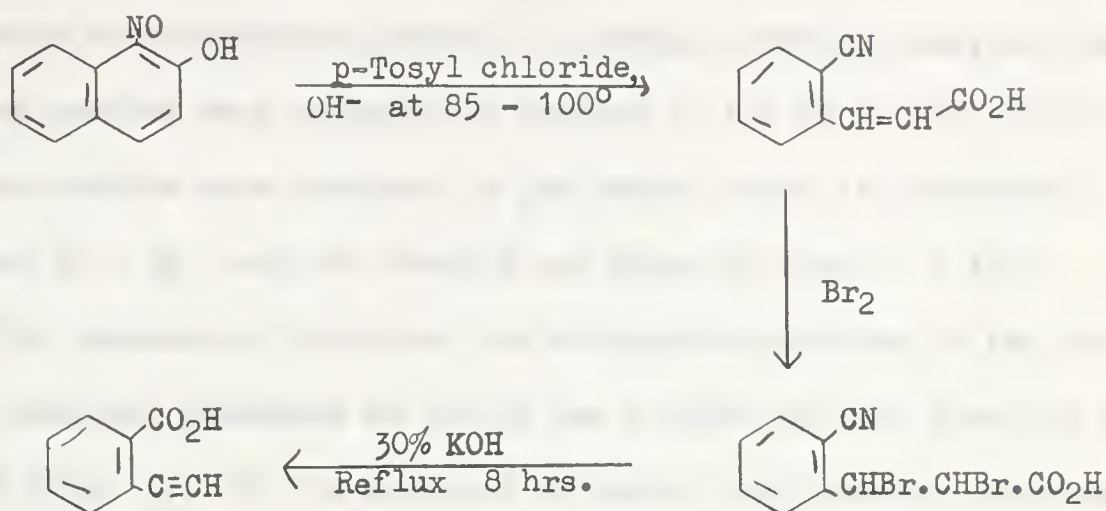
shown in the section describing the effects of pH on the reduction (See page 55). A further possible complication was discovered after this investigation had been in progress for about a year. Taube (28) reported that electron transfer can occur through a conjugated system involving a double bond and a carboxyl group. It was demonstrated that during the reduction of cobalt (III) pentamino methyl maleate by chromium (II) perchlorate, the ester was hydrolyzed, although hydrolysis did not occur under the reaction conditions in the absence of the reducing agent. More recently, Taube (29) has shown that the stereochemistry of the double bond is altered during the reaction, i.e. maleate is isomerised to fumarate. After these reductions the organic ligand is found complexed to the chromium (III) ion. In the phenylpropionic acid system, if electron transfer could occur through the carboxyl group, and if the reduction were also taking place independently of the carboxyl group, as is suggested by the observation that acetylene itself is reduced, then there would exist the possibility that two separate reactions were occurring, and their relative rates could be profoundly altered by changes in the pH of the solution. This would have been quite a serious complication, but there are two reasons for believing that it does not occur. If there were indeed an electron transfer through the carboxyl group, one would expect that one of the reaction products would be a stable chromium (III) cinnamate complex, since Taube (28,29) has isolated a similar complex in the case of the maleate transfer. In the case of the reduction of phenylpropionic acid however, no such complex has been observed, the only inorganic product being the hexaquo chromium (III) ion $\text{Cr}(\text{H}_2\text{O})_6^{+3}$ (See page 26). Thus electron transfer through the carboxyl group is

unlikely. It is rendered even less likely by the observation (page 56) that the phenylpropiolate anion is very much less active towards reduction by chromium (II) than is the undissociated acid. However, in order to eliminate the necessity for applying a correction factor to the rate values obtained in solutions of pH greater than 1.5, two acetylenic quaternary ammonium salts were prepared. These were N,N,N-trimethyl-(para-ethynylphenyl) ammonium chloride, and N,N,N-trimethyl-4-phenyl-3-butynyl ammonium chloride. (I and II). They were synthesised by the following series of reactions, which are described in the experimental section.



These salts are water soluble, and proved to react at rates which were conveniently measured in the pH ranges required. Two other organic substrates were synthesized for specific purposes, which are more conveniently described in the appropriate contexts. They were N,N,N-trimethyl-3-phenyl-2-propynyl ammonium chloride, and ortho-ethynylbenzoic acid. The former compound was prepared by a Mannich condensation between phenylacetylene, dimethylamine and formaldehyde,

as described by Mannich and Chang (30), and the latter, which was a new compound, was prepared by the following series of reactions.



(iii) THE ABSORPTION SPECTRA OF SOME OF THE CHROMIUM IONS
ENCOUNTERED DURING THE INVESTIGATION, AND THEIR DEPENDENCE ON pH

During the course of the investigation, it became necessary to know the absorption spectra of certain chromium ions, and how these spectra were affected by changes in the pH of the solution. These spectra were obtained in the manner which is described on pages 96 - 98 , and the results are shown in Figs. I - III.

In the presence of pyridine, the absorption spectrum of the chromium (II) ion remained unchanged as the pH was allowed to vary from 0.2 to 4.55 (Fig. I). In the presence of acetic acid however, although the spectrum obtained in solutions of higher acidity corresponded with that obtained in pyridine solutions, the spectrum changed as the pH increased (Fig. II). This suggests that as the concentration of acetate ion increases, a new species is formed, which is very probably the $\text{Cr}(\text{H}_2\text{O})_5(\text{OAc})^+$ ion. The spectrum of the hexaquo chromium (III) ion was not affected by changes in the pH of the solution up to a pH of 4.5, and the spectrum which has been obtained in this laboratory corresponds with that previously reported by Elving and Zemel (31).

The spectrum of the dinuclear ion obtained by the air oxidation of chromium (II) salts is affected by pH changes. Fig. III shows some of the spectra which were obtained in solutions of different pH, and Table IV gives the values of λ_{max} . and ϵ_{max} . which have been obtained.

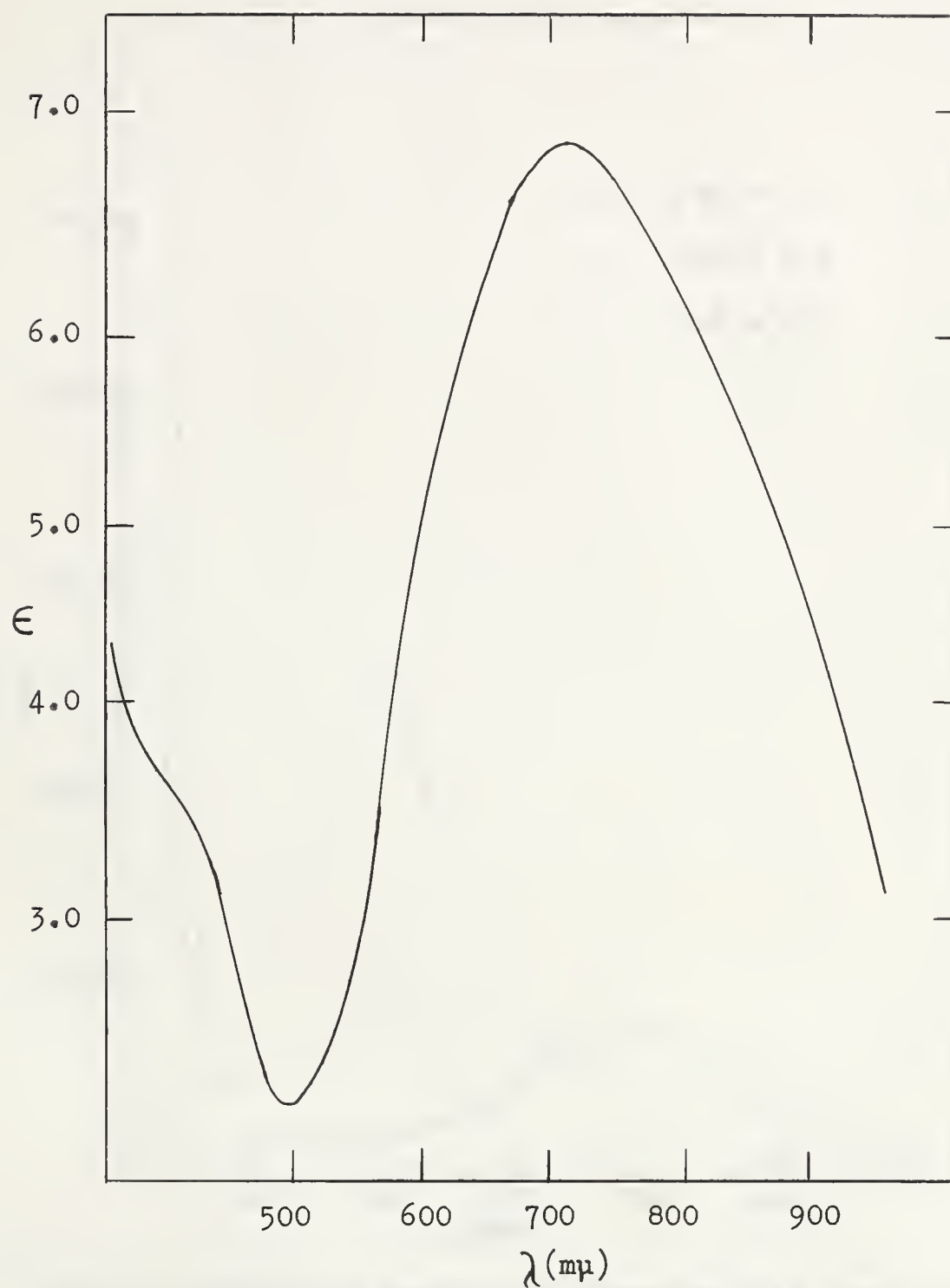


Fig. I Absorption Spectrum of Chromium (II) Perchlorate in the Presence of Pyridine in the pH Range 0.3 to 4.55

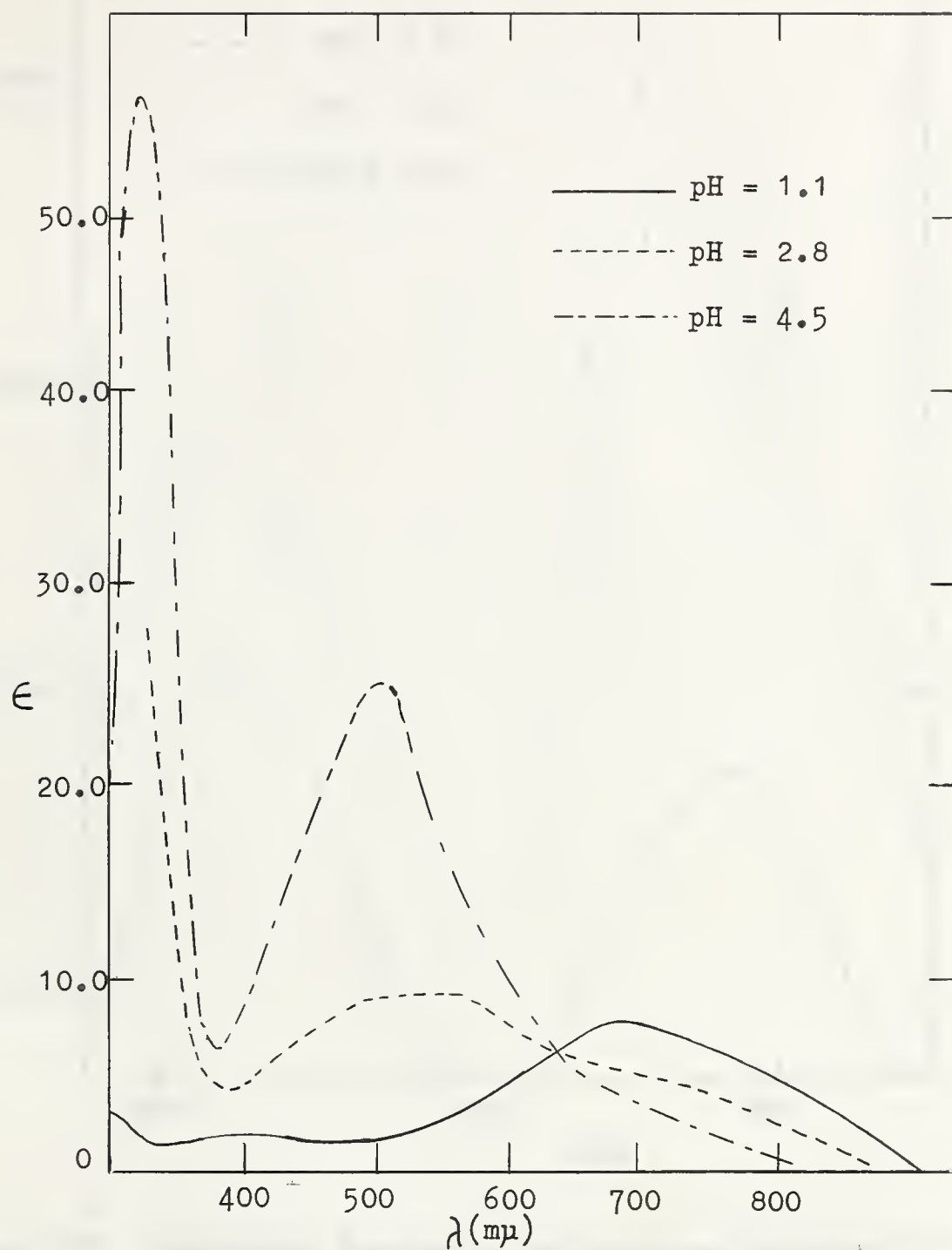


Fig. II Absorption Spectra of Chromium (II) Perchlorate in the Presence of Acetic Acid and Sodium Acetate in the pH Range 1.1 to 4.5

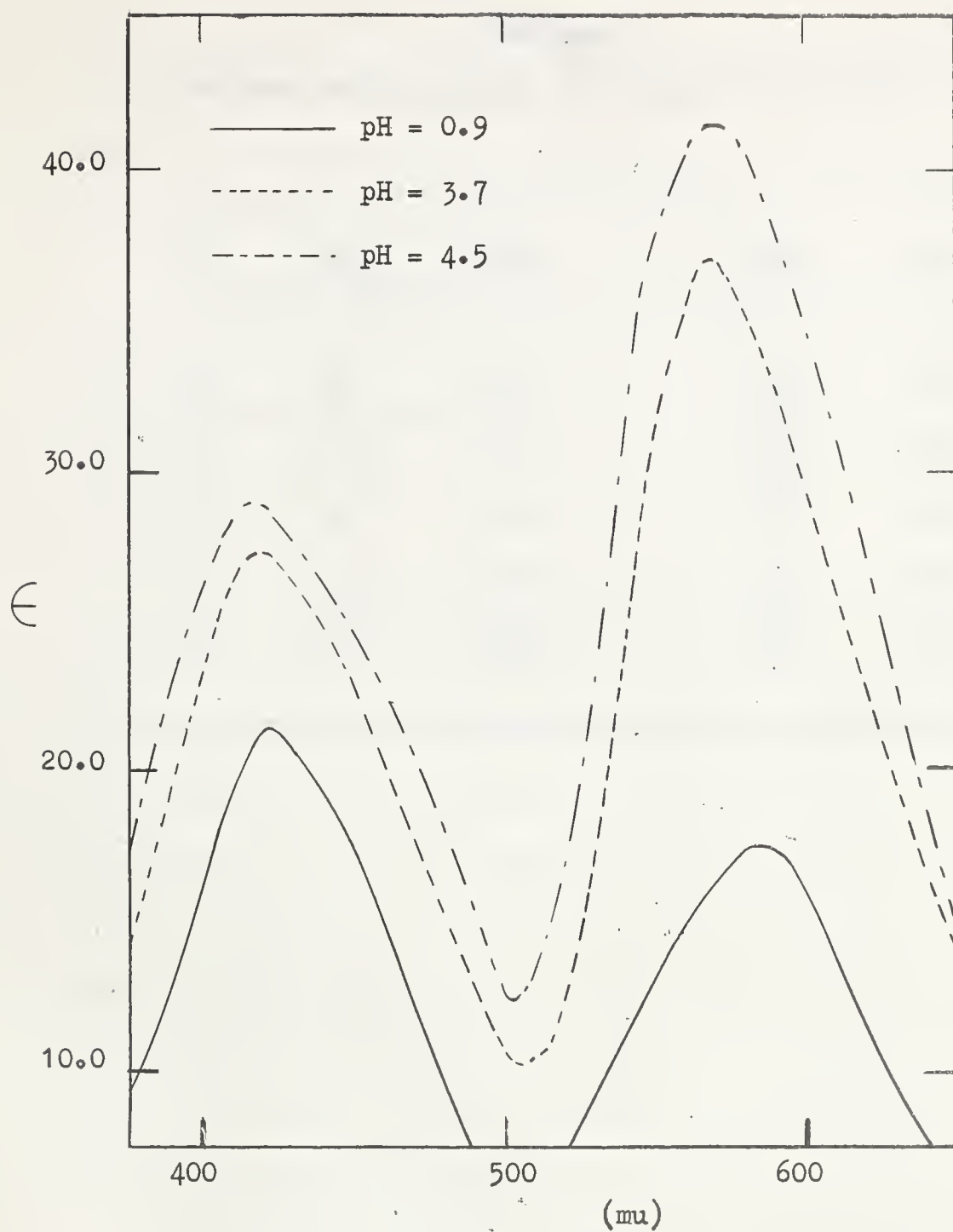


Fig. III Absorption Spectra of the Dinuclear Chromium (III) Ion
in the Presence of Sodium Acetate - Acetic Acid, in
the pH Range 0.9 - 4.5

TABLE IV

SPECTRAL VALUES FOR THE DINUCLEAR CHROMIUM (III) ION

pH	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}
0.9	420	21.7	585	17.8
3.2	417	21.2	570	33.0
3.7	418	27.6	567	37.3
4.1	418	28.8	567	40.0
4.5	417	28.9	567	41.4

(iv) THE NATURE OF THE PRODUCTS

a: The Organic Products - Rabinowitch and Looney (11) have shown that in the reduction of acetylene-d₂ with chromium (II) chloride, the product is mainly trans-ethylene-d₂, and they have used this method for the preparation of trans-ethylene-d₂ and trans-propene-d₁ from acetylene-d₂ and propyne-d₁ respectively.

R.I. Marsden (32) in this laboratory has isolated only trans-cinnamic acid from the reduction of phenylpropionic acid with chromium (II) chloride and chromium (II) sulphate, and has shown that cis-cinnamic acid is not isomerised under the conditions of the reaction.

For the reduction of trimethyl-4-phenyl-3-butyryl ammonium chloride, the infrared spectrum of the product corresponded with that of a trans-alkene, rather than with that of a cis-alkene. The spectrum of the cis-alkene was obtained for comparison purposes by reducing the alkyne with hydrogen, using Lindlar's palladium on charcoal catalyst, and the spectrum of the product exhibited the expected peak at 710 cm⁻¹ which is typical of a cis-substituted double bond (54). The spectrum of the product of reduction by chromium (II) had no peak in this region, but had an intense peak at 990 cm⁻¹, which is typical of a trans-substituted double bond.

The trans-reduction of acetylene-d₂ and propyne-d₁ shows that the stereochemistry of the product is controlled by a mechanistic process, rather than by the relative thermodynamic properties of the products, for in these cases, thermodynamic control would be expected to lead to an approximately 50:50 mixture of cis- and trans-products.

The only compound for which cis-reduction has been observed is N,N,N-trimethyl-3-phenyl-2-propynyl ammonium chloride. The reduction

was performed on a preparative scale, and the chromium (III) salts were removed by precipitation with ammonium hydroxide. The ultra-violet absorption spectrum of the neutralised filtrate was recorded and compared with the spectra of the cis- and trans-compounds (Fig. IV) which had been prepared by the known methods which are described on page 95. From the values given in Table V the ratio of cis- to trans-olefin in the product may be calculated to be 2.7:1. In order to determine whether any isomerisation of the olefinic product had occurred during the reaction or work up procedure, a control experiment was performed, in which a solution of the cis-olefin was allowed to stand in contact with excess chromium (II) perchlorate for twenty-four hours, and then isolated using the same procedure which was used for isolating the products of the reaction. The ultraviolet spectrum of the product in this case was identical with that of the initial cis-isomer, thus demonstrating that the appearance of the trans-olefin in the reduction product was caused by its formation during the reaction.

b: The Inorganic Products - The spectra reproduced in Figs. V, VI and VII indicate that for the reduction of phenylpropionic acid at pH values between 0.3 and 4.55, the chromium (III) product is not the dinuclear ion which has been described by Ardon and Plane (16). In solutions of high acidity, the product is the hexaquo chromium (III) ion (Fig, V). At higher pH values the spectrum of the product differs from the spectrum of the hexaquo chromium (III) ion, but the product is still evidently not the dinuclear ion. Since these spectra were obtained in the presence of sodium acetate and acetic acid, the chromium (III) ion actually formed is probably an acetato-

complex, since in the presence of high concentrations of acetate ion the chromium (II) salt is easily substituted, and the acetate ion in the coordination sphere of the chromium (II) ion will remain more firmly bound after the oxidation to chromium (III) has taken place. The fact that this ion was not observed when chromium (III) perchlorate was dissolved in solutions with high acetate concentration is a reflection on the inertness to ligand substitution of the chromium (III) ion.

No curves of the type shown in Figs. V to IX were obtained for the reduction of phenylpropionic acid in the presence of pyridine. However, there is a very distinct difference in colour between the dinuclear ion and the acetato-chromium (III) complex, which are green, and the hexaquo-chromium (III) ion, which is purple; and the solutions produced during the reduction of phenylpropionic acid in the pyridine - perchloric acid buffers had the distinctive purple colour over the entire pH range from 0.3 to 4.55, and it may be concluded that the inorganic product in these cases was the mononuclear hexaquo-chromium (III) ion.

TABLE V

SPECTRAL VALUES OF cis- AND trans-N,N,N-TRIMETHYL-3-PHENYL-2-PROPENYL
 AMMONIUM CHLORIDE, AND THE REDUCTION PRODUCT OF N,N,N-TRIMETHYL-
 3-PHENYL-2-PROPYNYL AMMONIUM CHLORIDE

Compound	$\lambda_{\text{max.}}$ (m μ)	$\epsilon_{\text{max.}}$	OD max.
<u>cis</u> -	275	12,500	
<u>trans</u> -	320	16,000	
Reduction	275	11,700	0.523
Product	320	4,800	0.215

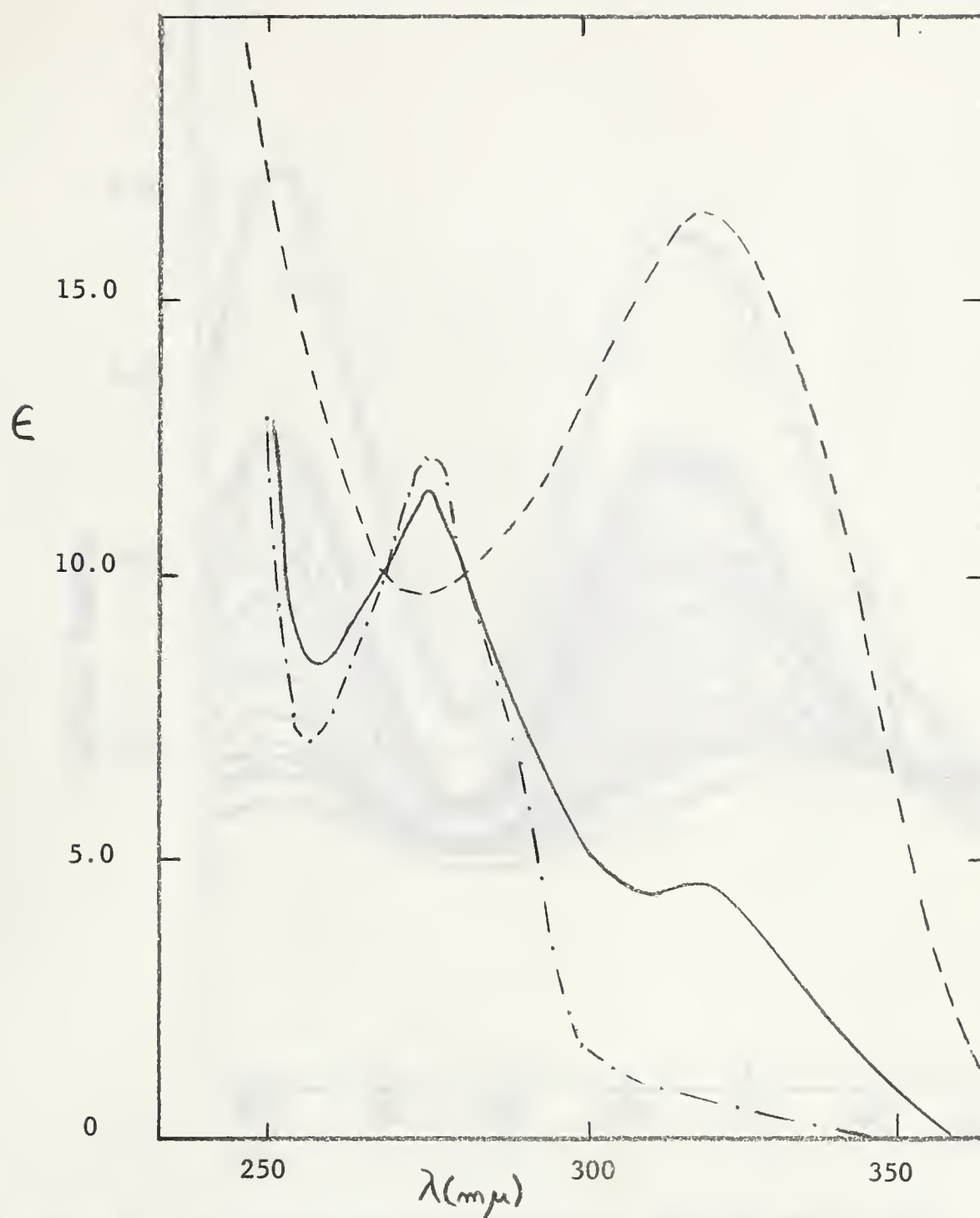


Fig. IV. Absorption Spectra of N,N,N-Triethyl-3-phenyl-2-propenyl ammonium chloride.

Legend

_____	Reduction Product
-----	<u>Trans</u> -isomer
-.-.-.-.-	<u>Cis</u> -isomer

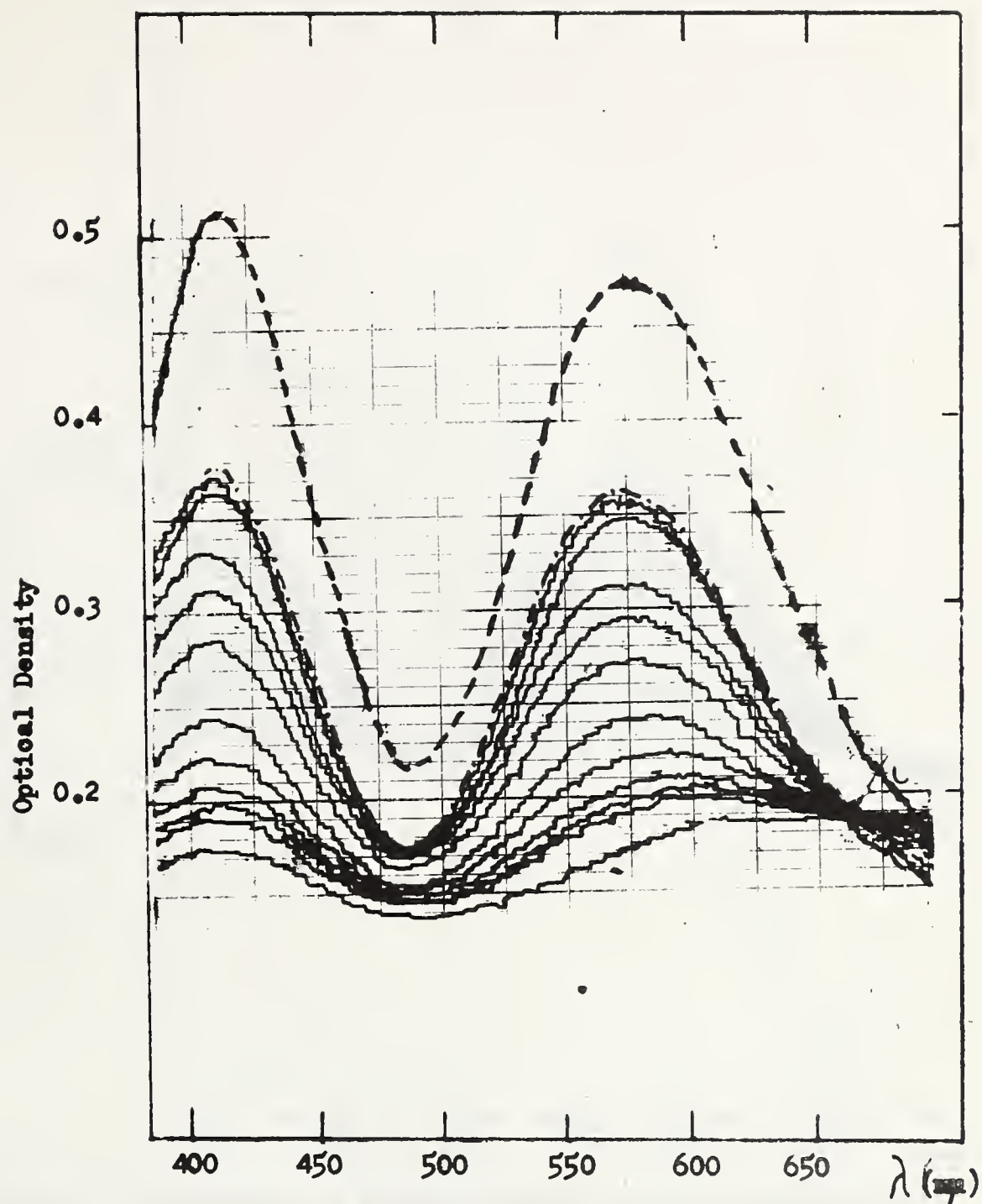


Fig. V Reduction of Phenylpropionic Acid by Chromium(II) Peroxide: Absorption Spectra at Different Times During the Reaction. pH = 1.1 Temperature = 25°

Legend: — Reaction Mixture; t_0 to t_∞
 - - - - - Calculated Absorption of $\text{Cr}(\text{H}_2\text{O})_6^{+++}$
 - - - - - Absorption of the Dinuclear Ion

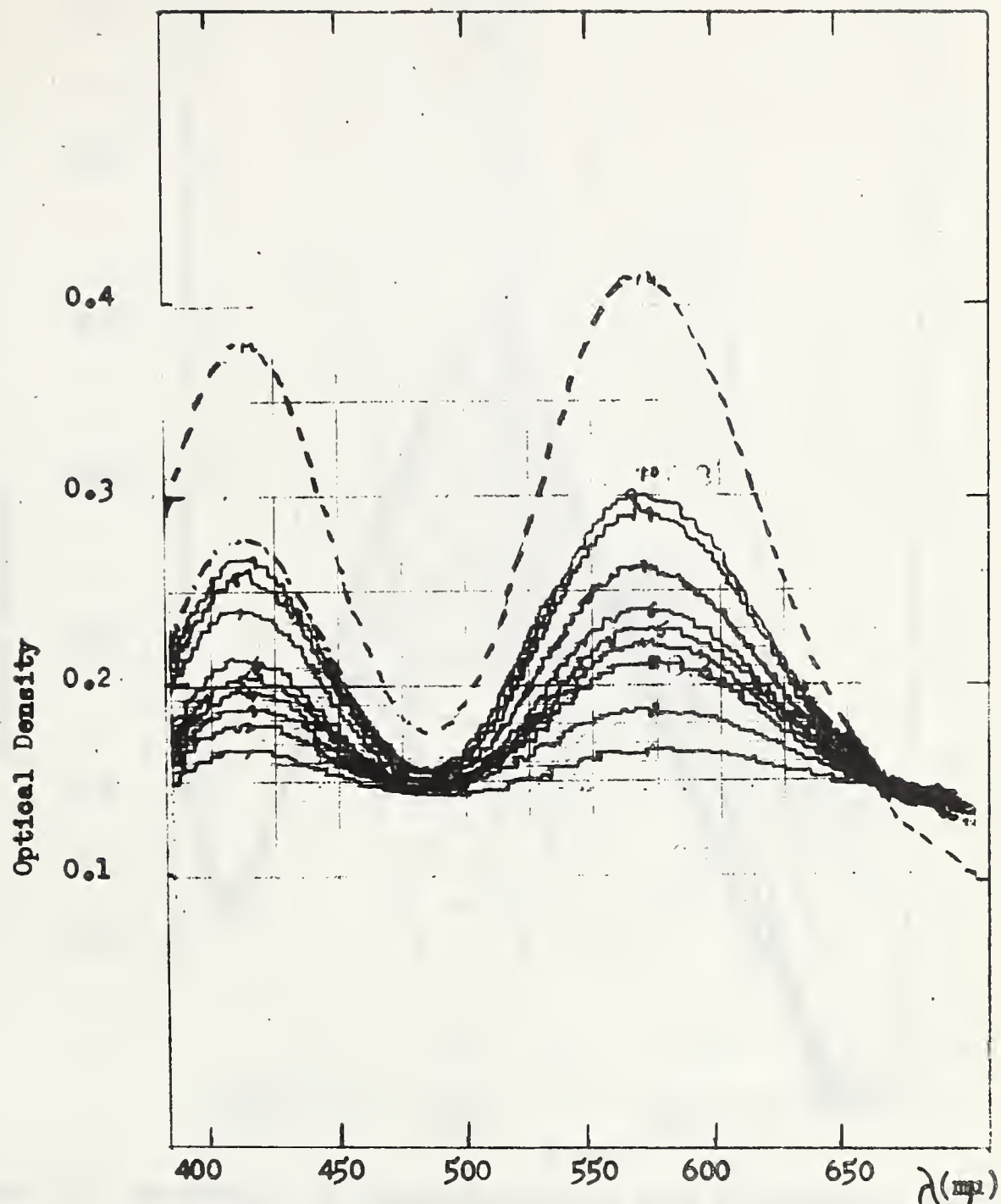


Fig. VI Reduction of Phenylpropionic Acid by Chromium(II) Perchlorate: Absorption Spectra at Different Times During the Reaction. pH = 2.4 Temperature = 25°

Legend: ——— Reaction Mixture; t_0 to t_{∞}
 - - - - - Calculated Absorption of $\text{Cr}(\text{H}_2\text{O})_6^{+++}$
 - · - · - Absorption of Dinuclear Ion

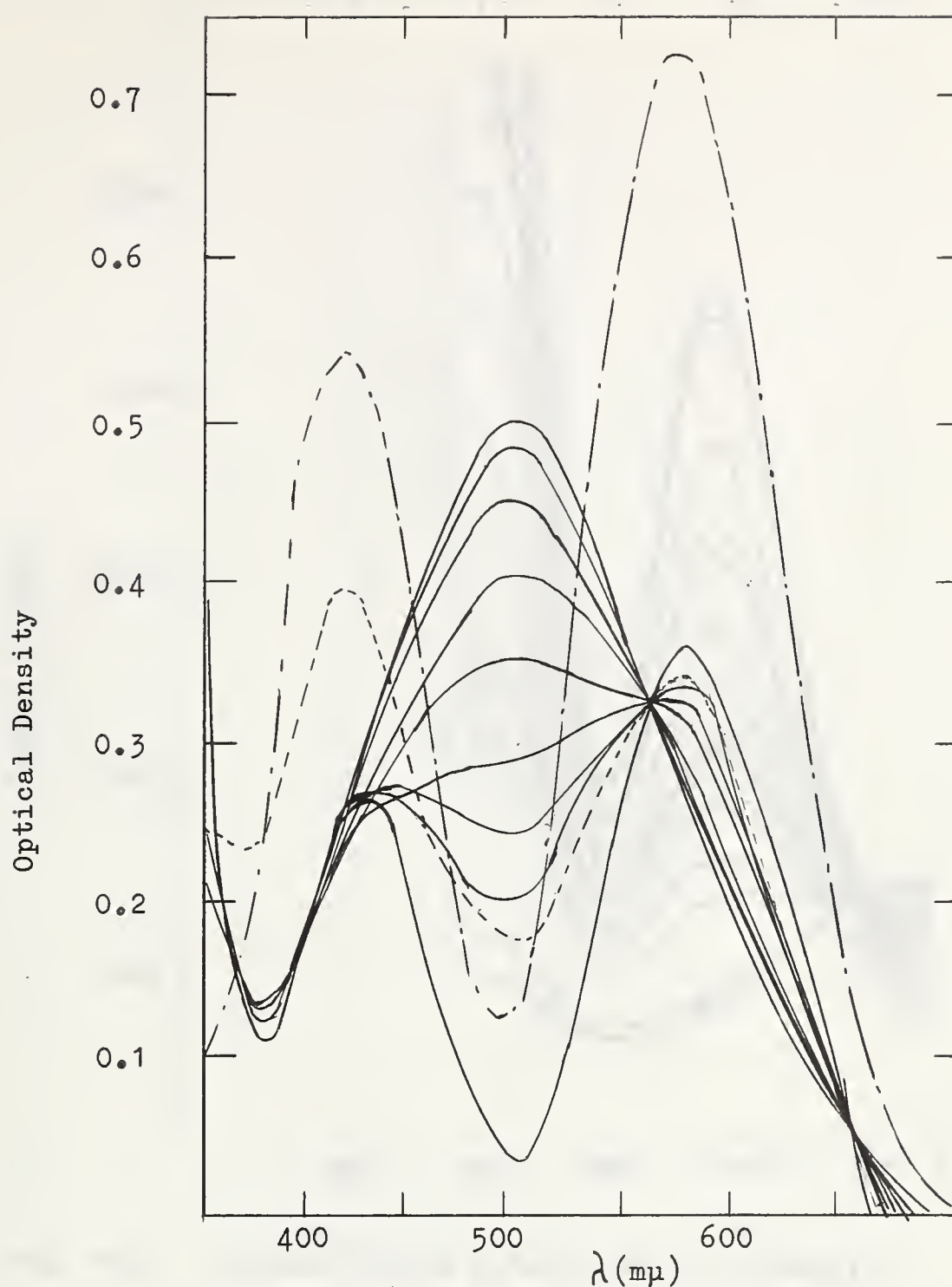


Fig. VII Reduction of Phenylpropionic Acid by Chromium (II) Perchlorate in the Presence of Sodium Acetate and Acetic Acid: Absorption Spectra at Different Times During the Reaction. pH = 4.2 Temperature = $25 \pm 0.5^\circ$

Legend

—————	Reaction Mixture, t_0 to t_{∞}
-----	Calculated Absorption of $\text{Cr}(\text{H}_2\text{O})_6^{+3}$
- - - - -	Absorption of Dinuclear Ion

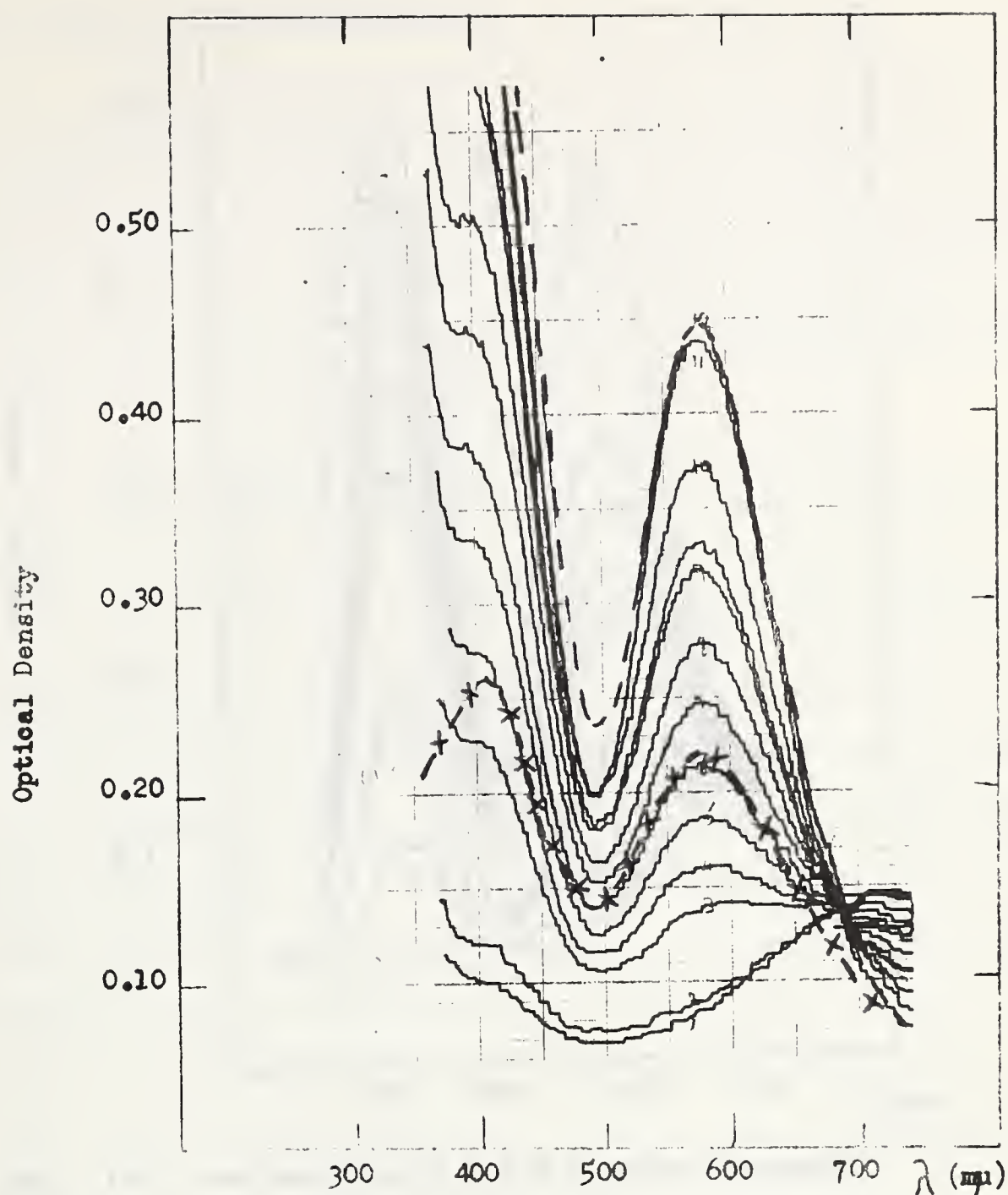


Fig. VIII The Reduction of N,N,N-Trimethyl-3-phenyl-2-propynyl Ammonium Chloride by Chromium (II) Perchlorate: Absorption Spectra at Different Times During the Reaction.

pH = 4.2 Temperature = $25 \pm 0.5^{\circ}$

Legend

- Reaction Mixture, t_0 to t_{∞}
- x-x-x- Calculated Absorption of $\text{Cr}(\text{H}_2\text{O})_6^{+++}$
- Absorption of the Dinuclear Ion

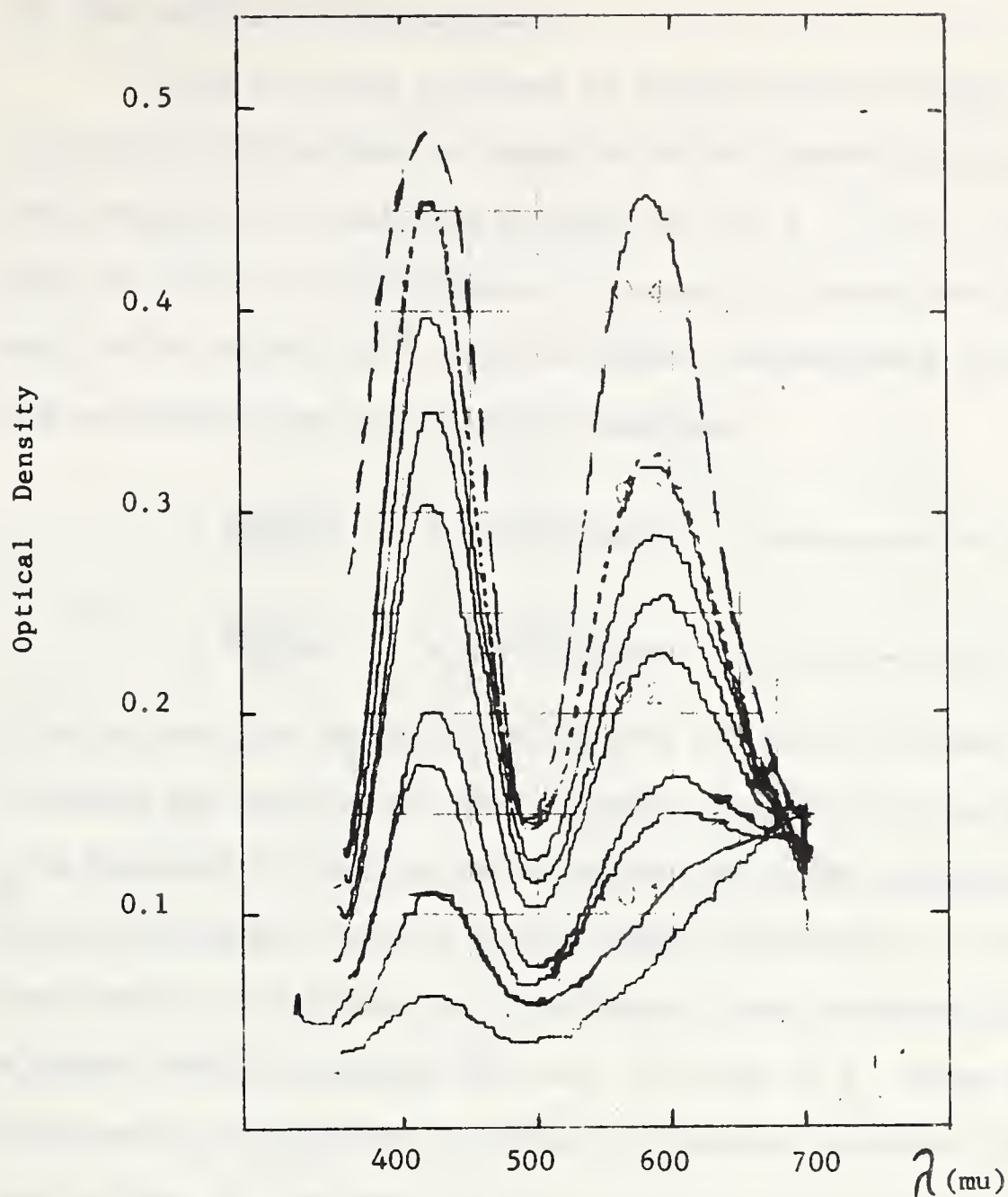


Fig. IX The Reduction of N,N,N-Trimethyl-4-phenyl-3-butynyl Ammonium Chloride by Chromium (II) Perchlorate: Absorption Spectra at Different Times During the Reaction

pH = 1.3 Temperature = $25 \pm 0.5^\circ$

Legend

———— Reaction mixture t_0 to t_∞
 ----- Calculated Absorption of $\text{Cr}(\text{H}_2\text{O})_6^{+++}$
 - - - - - Absorption of dinuclear Ion

(v) THE KINETICS OF THE REACTION

Three runs were performed at constant ionic strength, pH and acetic concentration, in which the initial concentration of phenylpropionic acid was kept constant at 1.35×10^{-3} mole. per litre, while the initial concentration of chromium (II) perchlorate was varied from 5.64 to 22.36×10^{-3} mole. per litre. Instantaneous rate coefficients were calculated from the following equations:

$$-\frac{d(\text{Cr}^{\text{II}})}{dt} = k_2(\text{Cr}^{\text{II}})(\text{Alkyne}) \text{ ----- } 1$$

$$-\frac{d(\text{Cr}^{\text{II}})}{dt} = k_3(\text{Cr}^{\text{II}})^2(\text{Alkyne}) \text{ ----- } 2$$

It may be seen from Table VI that k_2 does not have a constant value throughout any one run, and that it varies from run to run, but that k_3 is unchanged by changing the concentration of the chromium (II) ion. In fact the initial value of k_2 is directly proportional to the initial concentration of chromium (II) perchlorate, and consequently the reaction is second order in chromium (II) ion. The plot of k_2 versus the initial concentration of chromium (II) gives the expected straight line, as is shown in Fig. X, and the line has a slope of 4.08, which is in good agreement with the observed value of k_3 .

The order in phenylpropionic acid was established in much the same way, using a series of runs in which the initial concentration of chromium (II) perchlorate was kept constant, and the initial concentration of phenylpropionic acid was varied between 0.70 and 5.35×10^{-3} mole. per litre. The results, which are shown in Table VII and Fig. XI, show that the reaction is first order in phenylpropionic acid. The equations which

were used to calculate the rate coefficients in Table VII were:

$$-\frac{d(\text{Cr}^{\text{II}})}{dt} = k_2(\text{Cr}^{\text{II}})^2 \text{ ----- } 3$$

$$-\frac{d(\text{Cr}^{\text{II}})}{dt} = k_3(\text{Cr}^{\text{II}})^2(\text{Alkyne}) \text{ ----- } 4$$

Fig. XII shows a plot of the expression

$$4kt = \frac{x}{a(b-a)(a-x)} + \frac{2.303}{(b-a)^2} \log \frac{b(a-x)}{a(b-x)}$$

for a typical run, where $(a-x)$ is one half of the concentration of chromium (II) ion at time t , $(b-x)$ is the concentration of phenylpropionic acid and k is the reaction coefficient. The least squares line has been drawn through the points.

The reaction order was established in much the same way for the reduction of N,N,N-trimethyl-3-phenyl-2-propynyl ammonium chloride, and the results are shown in Table VIII.

Hence the rate expression for the reduction of alkynes by chromium (II) may be written:

$$-\frac{d(\text{Cr}^{\text{II}})}{dt} = k_3(\text{Cr}^{\text{II}})^2(\text{Alkyne}) \text{ ----- } 5$$

The rate of reduction is sensitive to changes in the dielectric nature of the solvent, and small salt, and solvent effects have been observed (Figs. XIII and XIV). The directions of these effects are those which would be expected for a reaction in which charge is increasing in the transition state, but no quantitative correlation has been attempted between the magnitudes of these effects and any possible reaction mechanisms.

Tables XI and XII show that neither light nor the presence of added chromium (III) ion has any effect on the rate.

TABLE VI

SECOND AND THIRD ORDER REACTION COEFFICIENTS FOR THE REDUCTION

OF PHENYLPROPIOLIC ACID BY CHROMIUM (II) PERCHLORATE

$$(\text{Alkyne})_0 = 1.36 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Ionic Strength} = 0.50$$

$$(\text{AcOH}) = 3.3 \text{ mole.l}^{-1}$$

$$\text{pH} = 1.75$$

$$\text{Temperature} = 45.0 \pm 0.05^\circ$$

Run	$10^3(\text{Cr}^{\text{II}})_0$ mole.l ⁻¹	$10^2 k_2 (1.\text{mole.l}^{-1} \text{sec}^{-1})$		$k_3 (1^2 \text{mole}^{-2} \text{sec}^{-1})$		
		(10%)	(75%)	(10%)	(75%)	(Least Squares)
E ₃	5.64	2.21	1.74	4.10	4.08	4.08
E ₅	13.62	5.50	5.01	4.05	4.05	4.05
E ₇	22.36	9.43	8.48	4.08	4.08	4.08

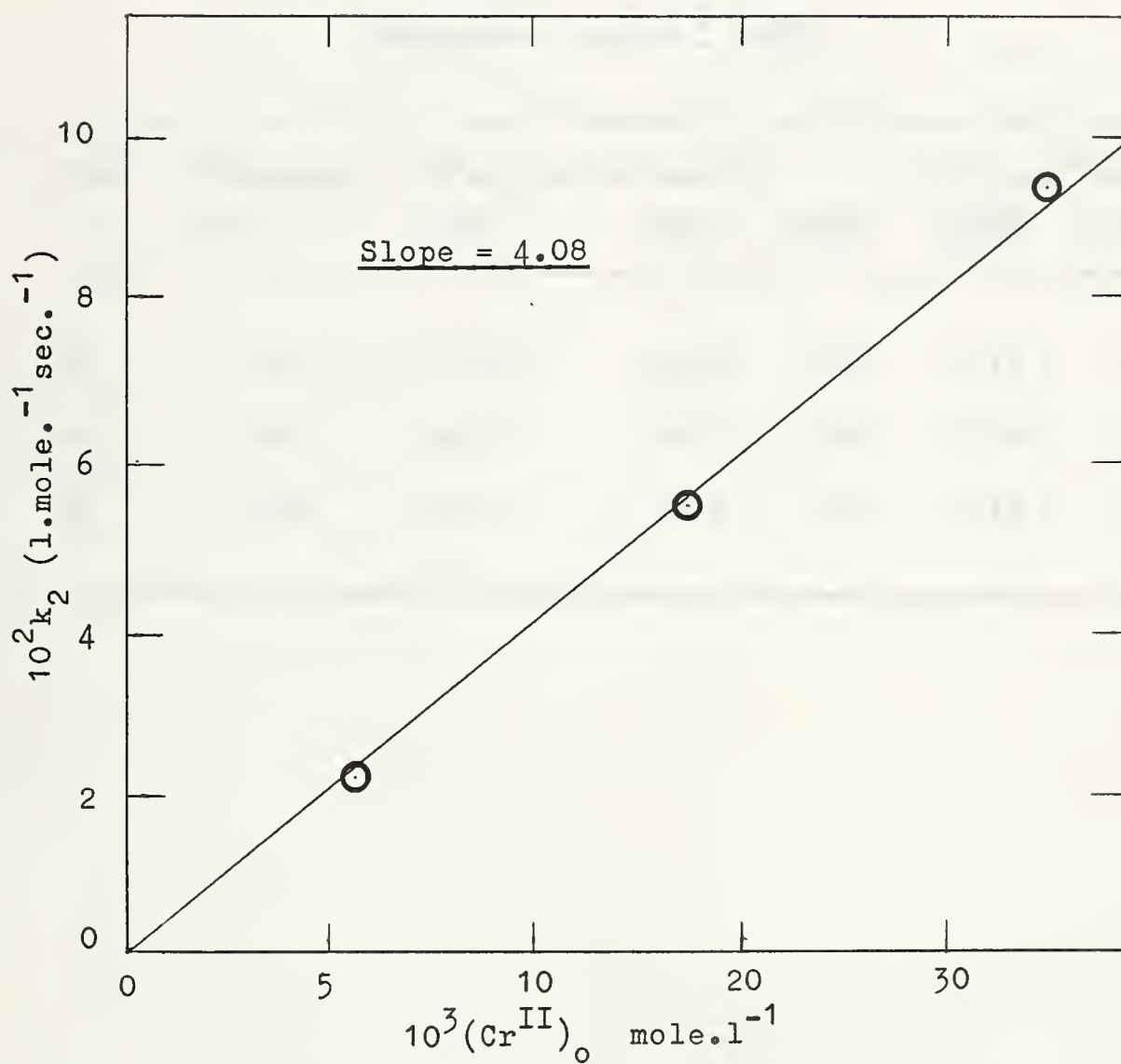


Fig. X Plot of $10^2 k_2$ versus $(Cr^{II})_0$ for the Reduction of Phenylpropionic Acid by Chromium (II) Perchlorate

TABLE VII

SECOND AND THIRD ORDER REACTION COEFFICIENTS FOR THE REDUCTION
OF PHENYLPROPIOLIC ACID BY CHROMIUM (II) PERCHLORATE

$(\text{Cr}^{\text{II}})_0 = 3.82 \times 10^{-3} \text{ mole.l}^{-1}$ Ionic Strength = 0.50

$(\text{AcOH}) = 1.6 \text{ mole.l}^{-1}$ pH = 1.40

Temperature = $45.0 \pm 0.05^\circ$

Run	$10^3(\text{Alkyne})_0$ mole.l ⁻¹	$10^4 k_2(1.\text{mole}^{-1}\text{sec}^{-1})$ (10%)	$10^4 k_2(1.\text{mole}^{-1}\text{sec}^{-1})$ (75%)	$k_3(10\%)$	$k_3(1^2\text{mole}^{-2}\text{sec}^{-1})$ (75%)	$k_3(1^2\text{mole}^{-2}\text{sec}^{-1})$ (Least Squares)
H ₁	0.70	7.92	4.00	1.17	1.16	1.16
H ₃	3.82	34.5	22.1	1.16	1.14	1.15
H ₅	5.35	61.1	48.9	1.16	1.14	1.15

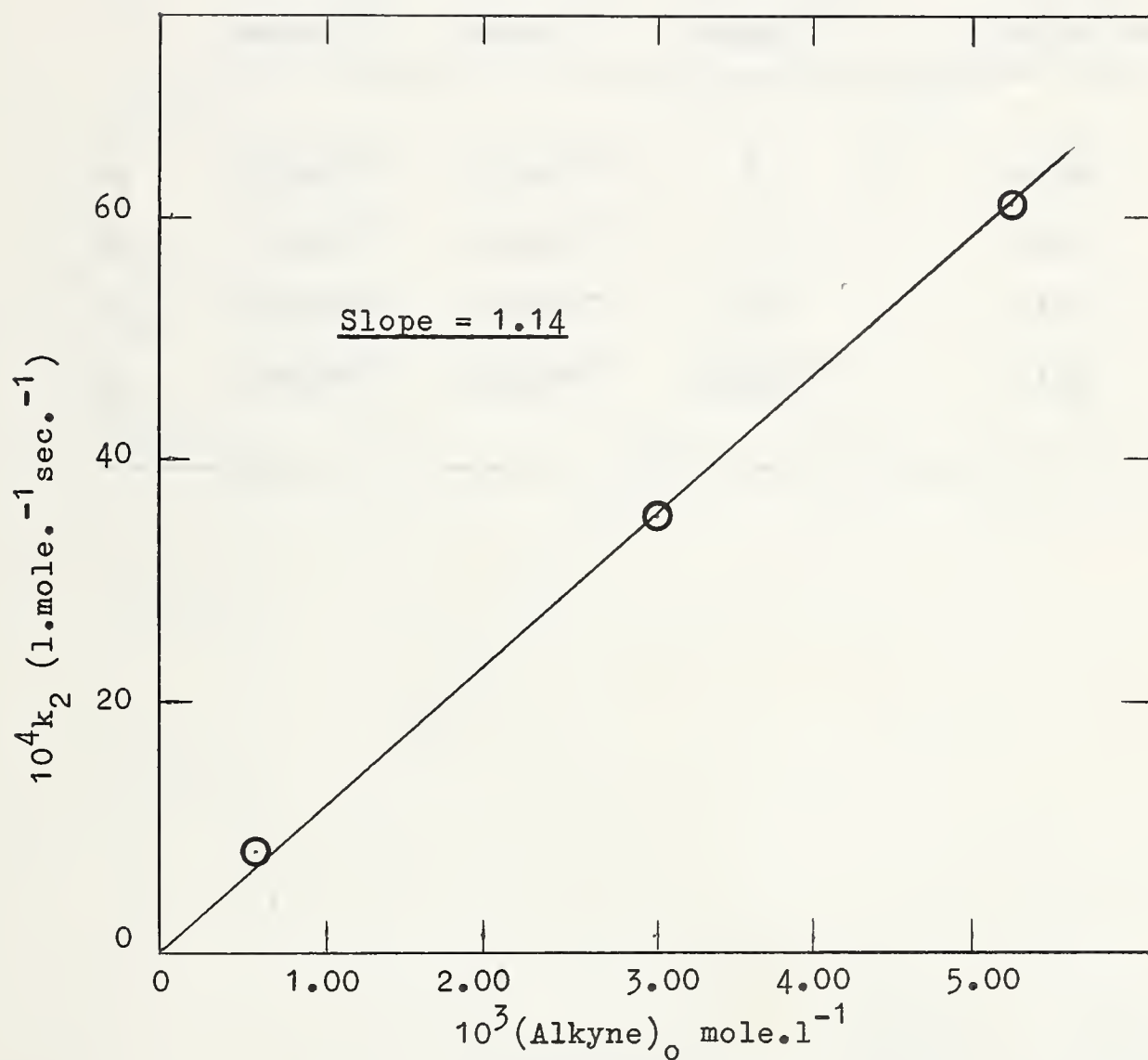


Fig. XI Plot of k_2 Versus $(\text{Alkyne})_0$ for the Reduction of Phenylpropionic Acid by Chromium (II) Perchlorate.

TABLE VIII

THIRD ORDER REACTION COEFFICIENTS FOR THE REDUCTION OF N,N,N-TRIMETHYL-
3-PHENYL-2-PROPYNYL AMMONIUM CHLORIDE BY CHROMIUM (II) PERCHLORATE

Temperature = $40.0 \pm 0.05^\circ$ pH = 4.20 Ionic Strength = 0.50

Run	(Alkyne) ₀ mole.l ⁻¹	(Cr ^{II}) ₀ mole.l ⁻¹	(Cr ^{III}) ₀ mole.l ⁻¹	k ₃ l ² mole ⁻² sec ⁻¹
R ₁	7.05x10 ⁻³	2.78x10 ⁻²	0	0.146
R ₂	1.10x10 ⁻²	2.78x10 ⁻²	0	0.144
N ₁₄	7.05x10 ⁻³	4.00x10 ⁻²	0	0.145
R ₃	1.10x10 ⁻²	2.78x10 ⁻²	3.0x10 ⁻²	0.149

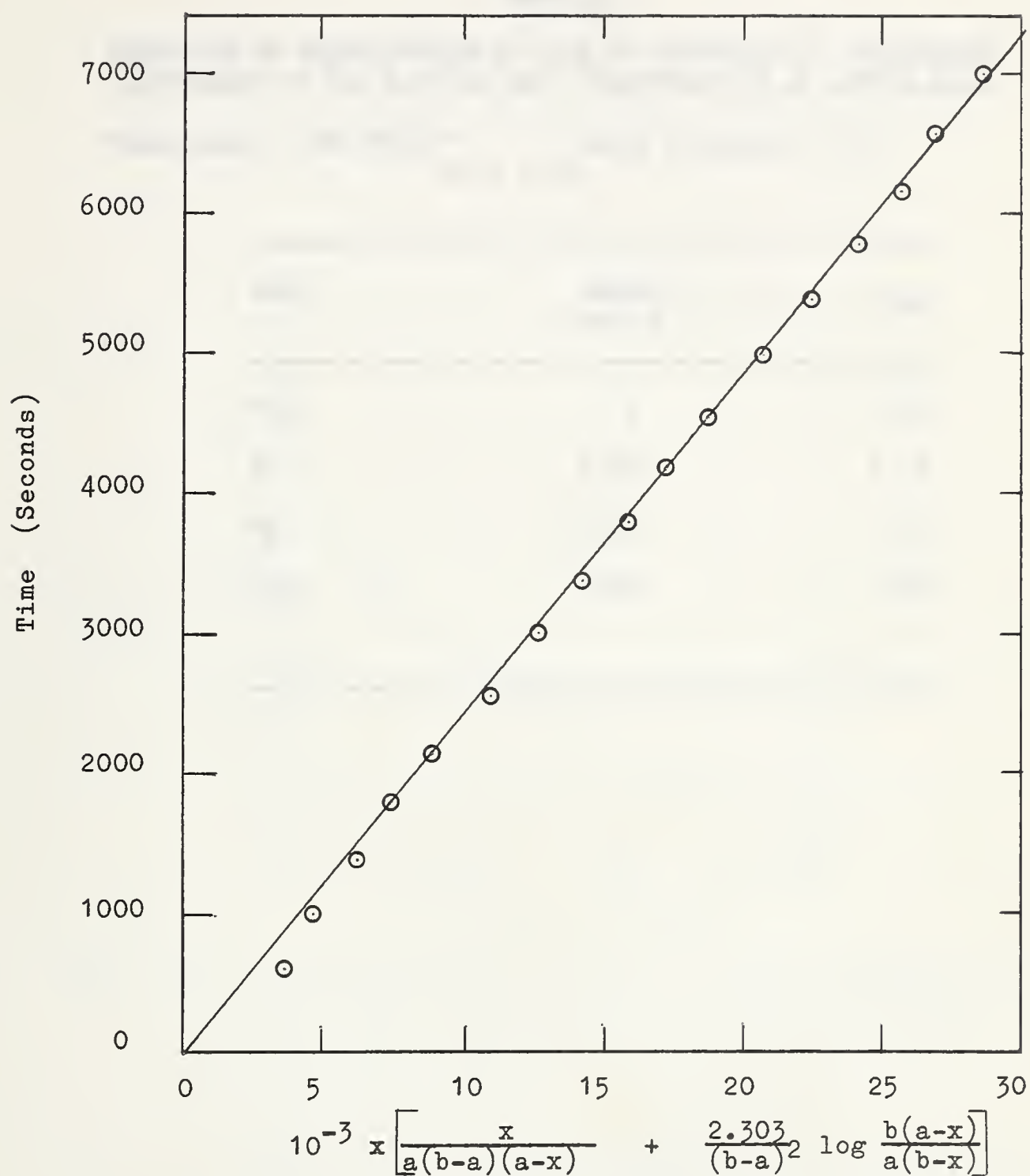


Fig. XI Run K_{13} . The Integrated Rate Expression Plotted as a Function of Time

TABLE IX

REDUCTION OF PHENYLPROPIOLIC ACID BY CHROMIUM(II) PERCHLORATE
DEPENDENCE OF THE RATE ON THE CONCENTRATION OF ACETIC ACID

Temperature = $40.0 \pm 0.05^\circ$ Ionic Strength = 0.5
pH = 1.40

Run	(AcOH) mole.l ⁻¹	k _{obs}
N ₁₅	0	1.34
K ₇	0.30	1.18
K ₈	0.70	1.11
K ₁₃	1.60	1.03

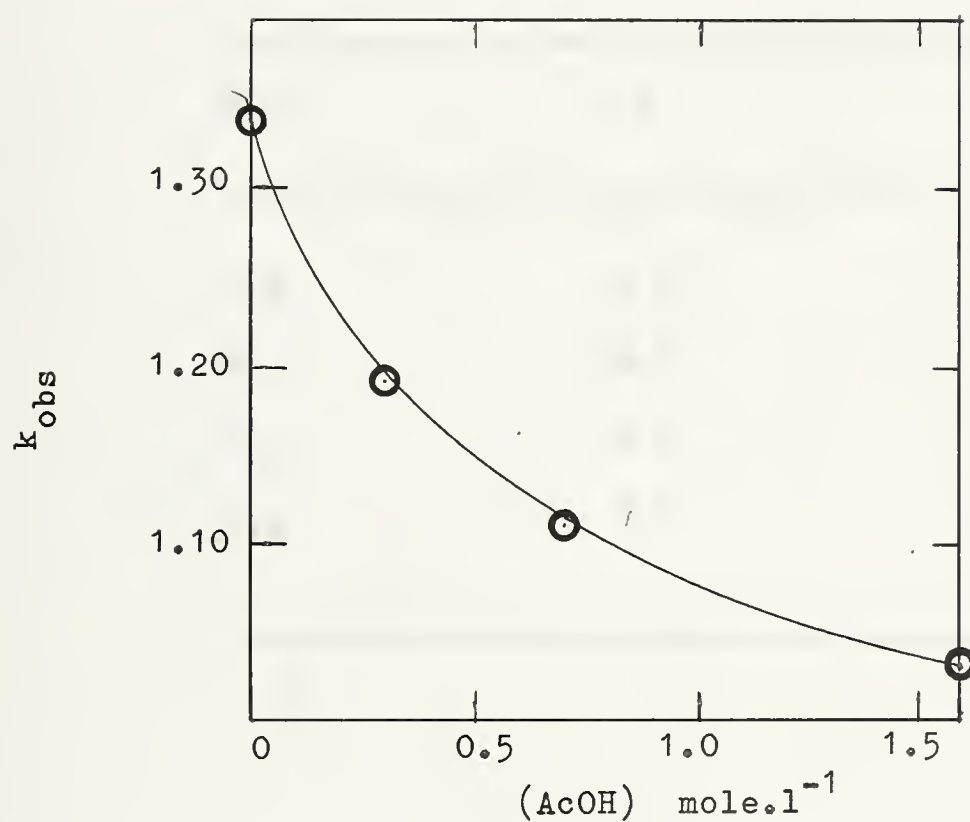


Fig. XIII Reduction of Phenylpropionic Acid by Chromium (II)
Perchlorate: The Effect of Acetic Acid Concentration
on the Rate.

Temperature = $40.0 \pm 0.05^\circ$

Ionic Strength = 0.50

pH = 1.40

TABLE X

REDUCTION OF PHENYLPROPIOLIC ACID BY CHROMIUM(II) PERCHLORATE
DEPENDENCE OF THE RATE ON THE IONIC STRENGTH

Temperature = $45.0 \pm 0.05^\circ$ (AcOH) = 1.6 mole.l^{-1}
pH = 1.40

Run	μ	k_{obs}
S ₁₀	1.2	1.25
S ₁₁	0.8	1.20
K ₅	0.5	1.17
S ₁₂	0.3	1.14

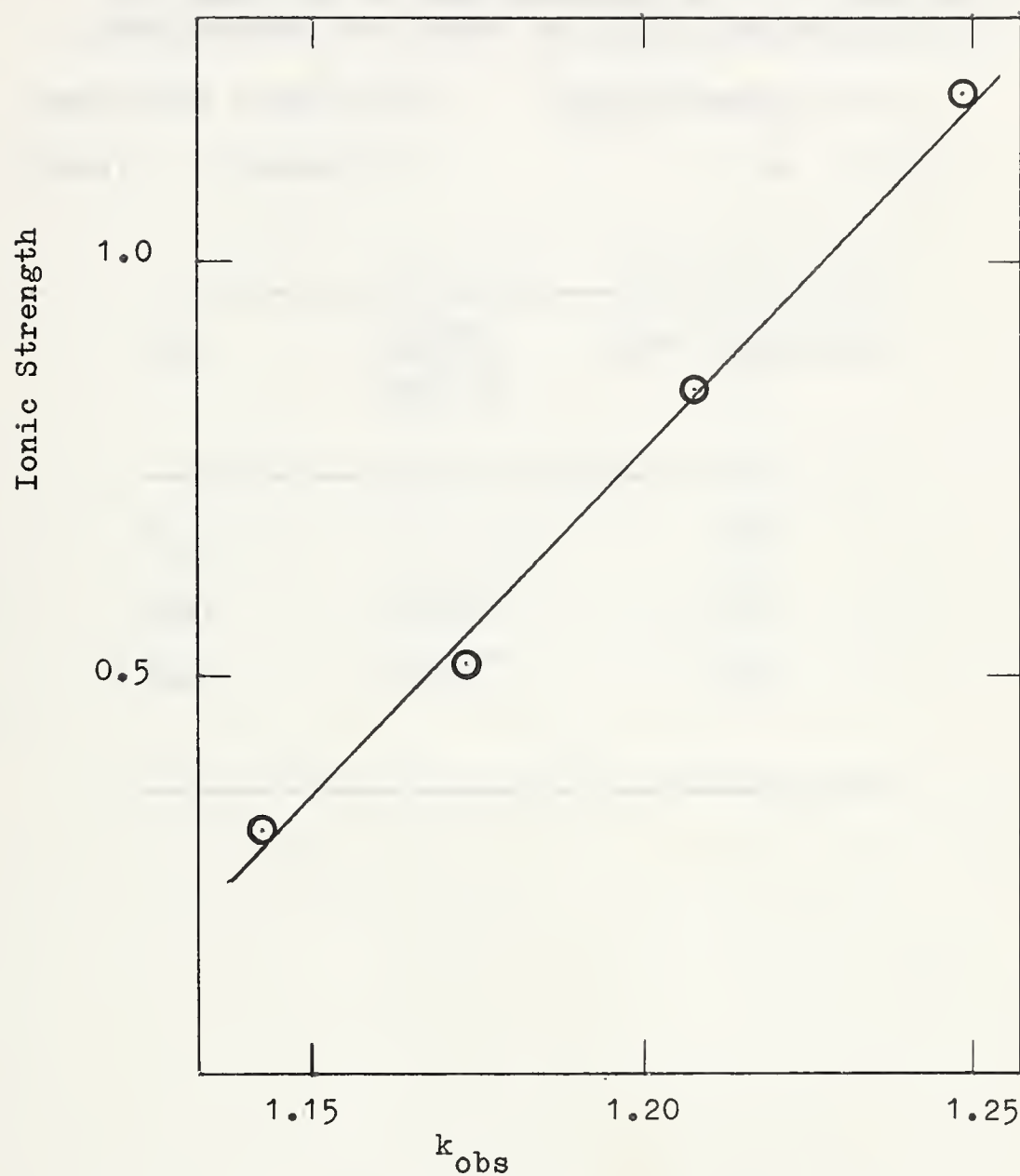


Fig. XIV. Reduction of Phenylpropionic Acid by Chromium (II)
 Perchlorate: The Effect of Ionic Strength on the Rate.
 Temperature = $45.0 \pm 0.05^\circ$ pH = 1.40
 $(\text{AcOH}) = 1.6 \text{ mole.l}^{-1}$

TABLE XI

THE REDUCTION OF PHENYLPROPIOLIC ACID BY CHROMIUM(II)
PERCHLORATE: THE EFFECT OF ADDED CHROMIUM(III) ION

Temperature = $40 \pm 0.05^\circ$

Ionic Strength = 0.5

(AcOH) = 1.6 mole.l^{-1}

pH = 1.40

Run	(Cr ^{III}) mole.l^{-1}	Rate Coefficient
K ₁₃	0	1.03
N ₂₃	2.8×10^{-2}	1.04
N ₂₄	8.7×10^{-2}	1.04

TABLE XII

THE REDUCTION OF PHENYLPROPIOLIC ACID BY CHROMIUM (II)

PERCHLORATE: THE EFFECT OF LIGHT ON THE RATE

Temperature = $40.0 \pm 0.05^\circ$

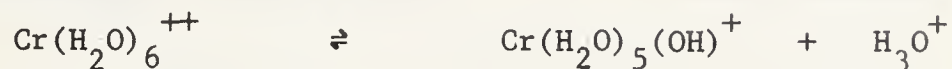
Ionic Strength = 0.50

pH = 1.40 (pyridine - perchloric acid)

Run	Conditions	Rate Coefficient
N ₁₅	Daylight	1.34
S ₃	Dark	1.34
S ₄	u.v. Lamp	1.33

(vi) THE EFFECT OF pH ON THE RATE

In view of the possible changes of the chromium (II) ions with pH, it was felt that a study of the effect of pH upon the observed reaction rate would be instructive.



The initial choice of substrate - phenylpropionic acid - causes difficulty in the assesment of the effect of pH upon the rate, and an analysis of this system was carried out.

Rate measurements were carried out in acetic acid - sodium acetate or in pyridine - perchloric acid buffers, or at low pH in a measured excess of perchloric acid such that the pH did not change markedly during the reaction. Values of pH above 1.0 were measured directly on a pH meter, and in solutions with pH below 1.0, the total strong acid concentration was measured by titration.

Trimethyl-(para-ethynylphenyl) ammonium chloride showed a linear rate dependence between pH values of 0.2 to 2.15, and trimethyl-4-phenyl-3-butyryl ammonium chloride showed a similar dependence in the pH range 1.45 to 3.0. One run was performed using the butynyl ammonium chloride at a pH of 4.2, but the reaction was so fast that the rate coefficient obtained cannot be regarded as reliable. However, the run is included in Table XIII and Fig. XV for the sake of completeness. The plot of log k versus pH is shown for these two salts in Fig. XV and it may be seen that both plots are linear, with slopes of about 1.3 to 1.4. Both of these salts were run in the pyridine buffers only, because as is seen from Fig. II, the chromium (II) ion changes its nature in the acetate buffers at higher pH values. This had the

TABLE XIII

THE REDUCTION OF N,N,N-TRIMETHYL-(p-ETHYNYLPHENYL) AMMONIUM CHLORIDE (I) AND N,N,N-TRIMETHYL-4-PHENYL-3-BUTYNYL AMMONIUM CHLORIDE (II): VARIATION OF RATE WITH pH

Temperature = $40.0 \pm 0.05^\circ$

Ionic Strength = 0.50

Run	Compound	pH	k_3	$\log k_3$
T ₃	I	0.20	0.31	-0.51
T ₄	I	0.75	1.56	0.19
T ₅	I	1.40	9.95	1.00
T ₆	I	1.85	39.8	1.60
T ₇	I	2.15	99.5	2.00
T ₈	II	1.45	0.24	-0.62
T ₉	II	1.80	0.75	-0.12
T ₁₀	II	2.20	3.03	0.48
T ₁₁	II	2.60	9.50	0.98
T ₁₂	II	3.20	38.0	1.56
T ₁₃	II	4.20	890	2.95

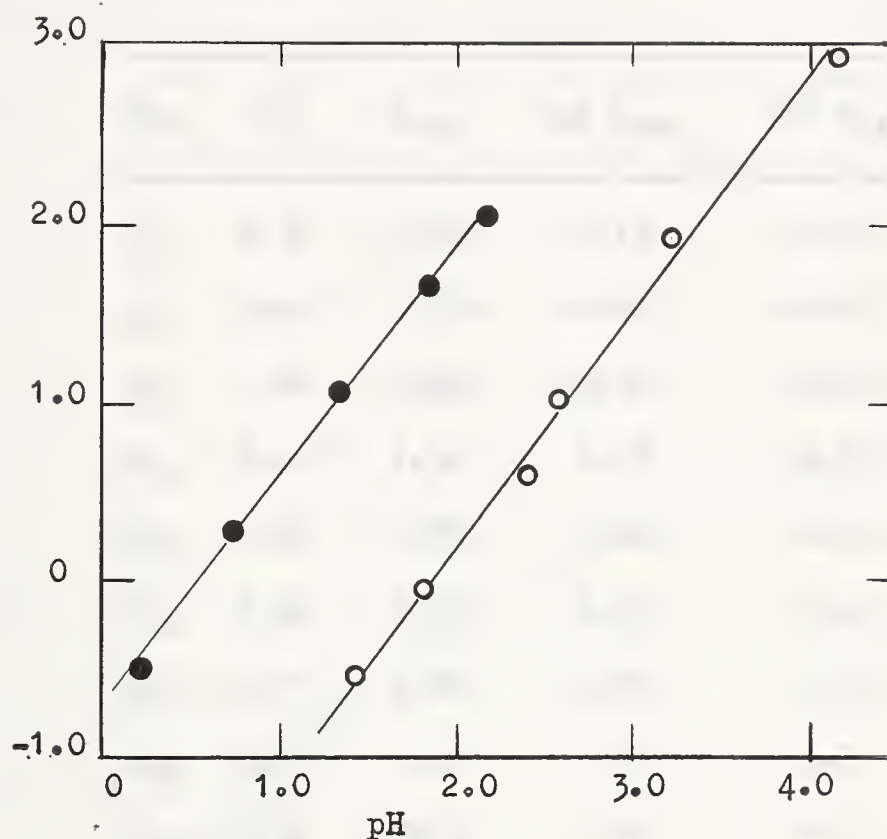


Fig. XV The Reduction of N,N,N-Trimethyl-(p-Ethynylphenyl) Ammonium Chloride and N,N,N-Trimethyl-4-Phenyl-3-Butynyl Ammonium Chloride by Chromium (II) Perchlorate: log k Plotted as a Function of pH

Legend

- N,N,N-Trimethyl-(p-Ethynylphenyl) Ammonium Chloride
- N,N,N-Trimethyl-4-phenyl-3-butynyl Ammonium Chloride

TABLE XIV

THE REDUCTION OF PHENYLPROPIOLIC ACID BY CHROMIUM (II) PERCHLORATE
IN THE PRESENCE OF PYRIDINE AND PERCHLORIC ACID: THE EFFECT OF
pH ON THE RATE

Temperature = $40.0 \pm 0.05^\circ$

Ionic Strength = 0.50

Run	pH	k_{obs}	$\log k_{\text{obs}}$	$\log k_{\text{HA}}$
Q ₁	0.30	0.065	-1.19	-1.19
Q ₂	0.50	0.126	-0.90	-0.89
Q ₃	1.00	0.498	-0.30	-0.28
N ₁₅	1.40	1.34	0.13	0.18
N ₂₁	1.50	1.90	0.28	0.35
N ₂₂	1.60	2.14	0.33	0.42
N ₁₇	2.30	8.36	0.92	1.02
N ₁₈	3.05	21.4	1.33	2.21
N ₁₉	3.45	34.3	1.54	2.77
N ₁₆	4.20	49.5	1.69	3.66
N ₂₀	4.55	65.8	1.82	4.14
T ₂	5.65	120	2.08	5.50

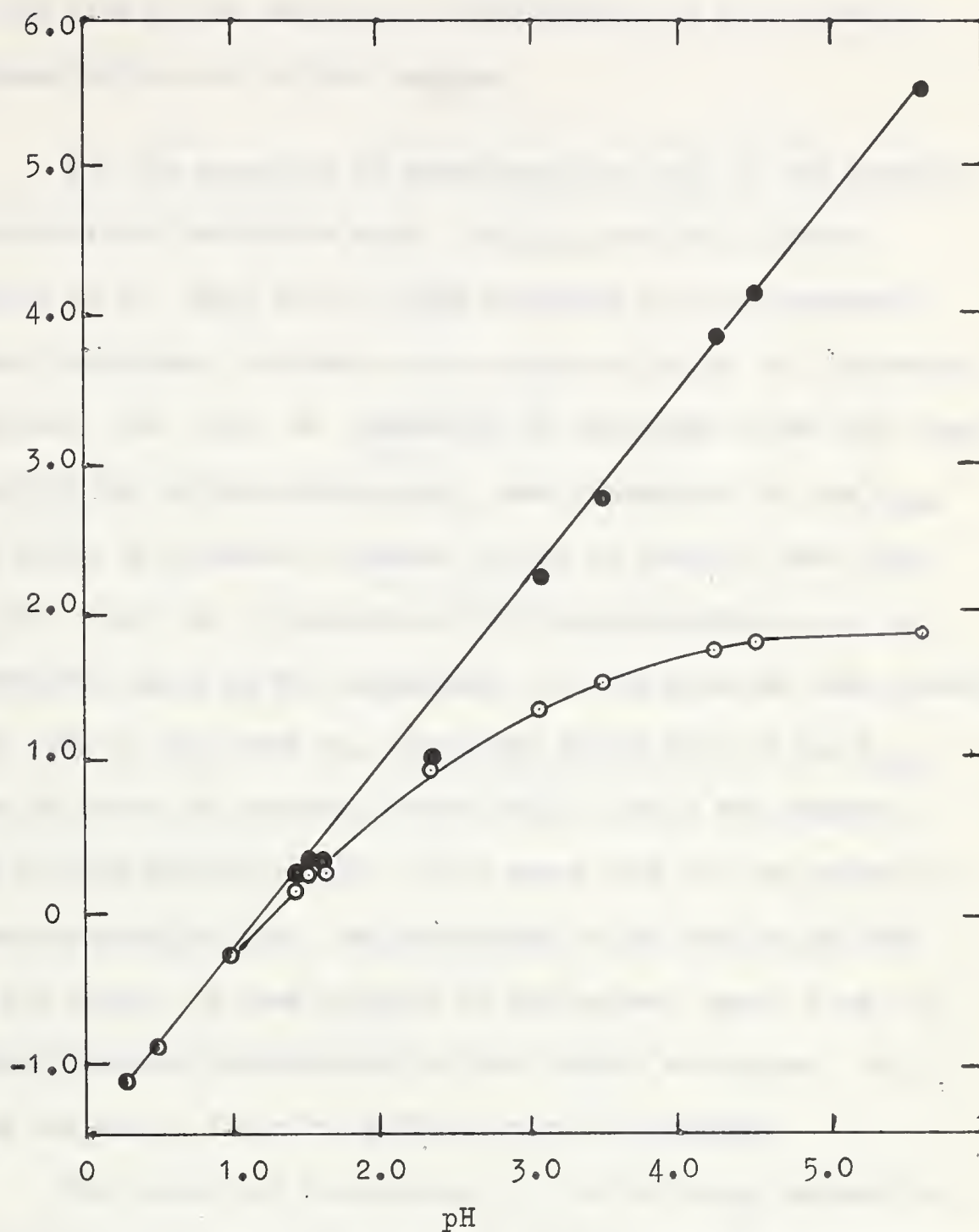


Fig. XVI The Reduction of Phenylpropionic Acid by Chromium (II)

Perchlorate: $\log k_{\text{obs}}$ and $\log k_{\text{HA}}$ Plotted as

Functions of pH

- Legend
- $\log k_{\text{obs}}$
 - $\log k_{\text{HA}}$
 - $\log k_{\text{obs}}$ and $\log k_{\text{HA}}$

effect of complicating the situation still further, as may be seen from the case of the reduction of phenylpropionic acid which is discussed at the end of this section.

For the reduction of phenylpropionic acid in the presence of pyridine and perchloric acid, $\log k_{\text{obs}}$ was not a linear function of pH (Fig. XVI). This behaviour is to be expected because the organic substrate dissociates as the pH is increased, and unless the rate of reduction of the anion were the same as that of the undissociated acid, some dependence of $\log k_{\text{obs}}$ on pH would be expected. However, it may be readily seen from Fig. XVI that the dissociation of phenylpropionic acid is not the only cause of the dependence of the observed rate constant on pH, for if this were so, the slope of the plot of $\log k_{\text{obs}}$ versus pH could not possibly exceed unity, while the observed slope at high acidity is 1.3. This means that for the reduction of phenylpropionic acid, the dependence of the rate on pH must have its origin in some property of the system apart from the changing degree of dissociation of the organic substrate, and it may be the sum of these two effects which is observed.

The system may be subjected to the following mathematical analysis, where the symbols used have the following connotations: HA represents phenylpropionic acid, $(\text{HA})_{\text{T}}$ is the total concentration of HA, (HA) is the concentration of the undissociated acid, and (A^-) is the concentration of the anion: k_{HA} is the rate coefficient for the reduction of the undissociated acid at a specified pH, and k_{A^-} is the rate coefficient for the reduction of the anion.

The rate expression

$$\text{Rate} = k_{\text{obs}}(\text{Cr}^{\text{II}})^2(\text{HA})_{\text{T}} \quad \text{-----} \quad 5$$

may be written

$$\text{Rate} = k_{\text{HA}}(\text{Cr}^{\text{II}})^2(\text{HA}) + k_{\text{A}^-}(\text{Cr}^{\text{II}})^2(\text{A}^-) \quad \text{----} \quad 5a$$

The dissociation constant of phenylpropionic acid

$$K = \frac{(\text{H}^+)(\text{A}^-)}{(\text{HA})} \quad \text{-----} \quad 6$$

may be written

$$K = \frac{(\text{H}^+)(\text{A}^-)}{(\text{HA})_{\text{T}} - (\text{A}^-)} \quad \text{-----} \quad 6a$$

from which is obtained the expression

$$(\text{A}^-) = (\text{HA})_{\text{T}} \frac{K}{(\text{H}^+) + K} \quad \text{-----} \quad 7$$

Equation 6) may also be written

$$K = \frac{(\text{H}^+)[(\text{HA})_{\text{T}} - (\text{HA})]}{(\text{HA})} \quad \text{-----} \quad 6b$$

from which we obtain the expression

$$(\text{HA}) = (\text{HA})_{\text{T}} \frac{(\text{H}^+)}{(\text{H}^+) + K} \quad \text{-----} \quad 8$$

and substituting 7) and 8) into 5a), we obtain

$$\text{Rate} = (\text{Cr}^{\text{II}})^2(\text{HA})_{\text{T}} \frac{(\text{H}^+)k_{\text{HA}} + Kk_{\text{A}^-}}{(\text{H}^+) + K} \quad \text{-----} \quad 9$$

Combining equations 9) and 5), we obtain for k_{obs} that,

$$k_{\text{obs}} = \frac{(\text{H}^+)k_{\text{HA}} + Kk_{\text{A}^-}}{(\text{H}^+) + K} \quad \text{-----} \quad 10$$

But since k_{HA} and k_{A^-} are rate coefficients for processes which are themselves dependent on pH, we may write

$$k_{\text{HA}} = \frac{k_{\text{HA}_0}}{(\text{H}^+)^{\alpha}}, \quad \text{and} \quad k_{\text{A}^-} = \frac{k_{\text{A}_0^-}}{(\text{H}^+)^{\alpha}}$$

from which equation 10) becomes

$$k_{\text{obs.}} = \frac{(H^+)k_{\text{HAO}} + Kk_{\text{AO}^-}}{(H^+)^{\alpha} [(H^+) + K]} \quad \text{-----} \quad 11$$

By taking the logarithm of equation 11 and differentiating twice with respect to pH, we obtain that the pH at the inflexion point of the plot of $\log k_{\text{obs.}}$ versus pH is given by the expression:

$$(pH)_{\text{infl.}} = pK - \frac{1}{2} \log \frac{k_{\text{AO}^-}}{k_{\text{HAO}}} \quad \text{-----} \quad 12$$

We have been unable to extend the range of experimental observations to include the pH at the inflexion point, but the results reported in Table XIV and shown in Fig. XVI show that the inflexion point does not lie within ± 2 pH units of the value for pK, which is 2.24 (Ref. 34).

Hence, from equation 12, either $k_{\text{HAO}} > 10^4 k_{\text{AO}^-}$, or $k_{\text{AO}^-} > 10^4 k_{\text{HAO}}$.

The present experimental results are not sufficiently extensive for a choice to be made with any certainty between these two possibilities, but what evidence there is seems to suggest that the former is correct. If the reaction involves the transfer of an electron or a hydride ion to the triple bond in the rate determining step, it would be expected that such a transfer to a neutral molecule - the undissociated acid - would be faster than to a negatively charged ion - the acid anion.

further evidence in favour of k_{HAO} being greater than k_{AO^-} comes from a calculation of the value of the slope at the inflexion point in terms of α , the order of dependence on hydronium ion concentration.

If $k_{\text{HAO}} > k_{\text{AO}^-}$, the slope at the inflexion point is given by the expression, $(\text{Slope})_{\text{infl.}} > \alpha - 1$, and equation 12) predicts that

the inflexion point will occur at a pH which is greater than 2.24. The minimum slope which has been observed at high pH values is 0.3, and thus we may write, $0.3 \gg \alpha - 1$, from which $\alpha \ll 1.3$.

However, if $k_{HA_0} < k_{A_0^-}$, the slope at the inflexion point is given by the expression, $(\text{Slope})_{\text{infl.}} \ll 1 + \alpha$, and in this case equation 12) predicts that the inflexion point will occur at a pH which is less than 2.24. The maximum slope which has been observed at low pH values is 1.3, and thus we may write in this instance, $1.3 \ll 1 + \alpha$, from which $\alpha \gg 0.3$. It seems more reasonable that the value of α should be 1.3 rather than 0.3 because both of the quaternary ammonium salts show a slope of 1.3 when the logarithm of their observed rate coefficients are plotted versus pH (Fig. XV), and if phenylpropionic acid were being reduced by the same mechanism, the dependence of the rate coefficient on hydronium ion concentration would be expected to be of a similar value.

The reduction of phenylpropionic acid was also studied using acetic acid - sodium acetate buffers. Fig. XVII shows that $\log k_{\text{obs}}$ has a more complicated dependence on pH than in the pyridine - perchloric acid system, and that $\log k_{HA}$ is linear with pH only below pH values of 2.5, and falls away from the linear plot at higher pH values. This may be because the reducing agent changes its nature at the higher pH values (See Fig. II), and the ion which is formed at high concentrations of acetate ion is a less powerful reducing agent than the hexaquo-chromium (II) ion. Although the nature of the chromium (III) product has not been definitely established at the higher pH values in acetic acid - sodium acetate buffers, it seems likely that it would be the

$\text{Cr}(\text{H}_2\text{O})_5(\text{AcO})^{+2}$ ion. The spectrum of the product differs from that of the hexaquo chromium (III) ion (Fig. VII), and since chromium (II) is labile to ligand substitution, whereas chromium (III) is not, the acetate ion could easily enter the coordination sphere of the chromium (II) ion and after oxidation to chromium (III) it would remain firmly bound.

TABLE XV

THE REDUCTION OF PHENYLPROPIOLIC ACID BY CHROMIUM (II) PERCHLORATE
IN THE PRESENCE OF ACETIC ACID AND SODIUM ACETATE: THE EFFECT OF

pH ON THE RATE

Temperature = $40.0 \pm 0.05^\circ$

Ionic Strength = 0.50

(AcOH) = 1.6 mole.l^{-1}

Run	pH	k_{obs}	$\log k_{\text{obs}}$	$\log k_{\text{HA}}$
S ₈	0.3	0.05	-1.30	-1.29
S ₇	0.5	0.10	-1.00	-0.99
S ₉	1.0	0.39	-0.41	-0.39
K ₁₃	1.4	1.03	0.01	0.07
S ₅	2.1	6.31	0.80	0.91
K ₁₁	2.85	17.5	1.24	1.95
S ₄	3.6	10.7	1.03	2.41
L ₂	4.3	4.20	0.62	2.69

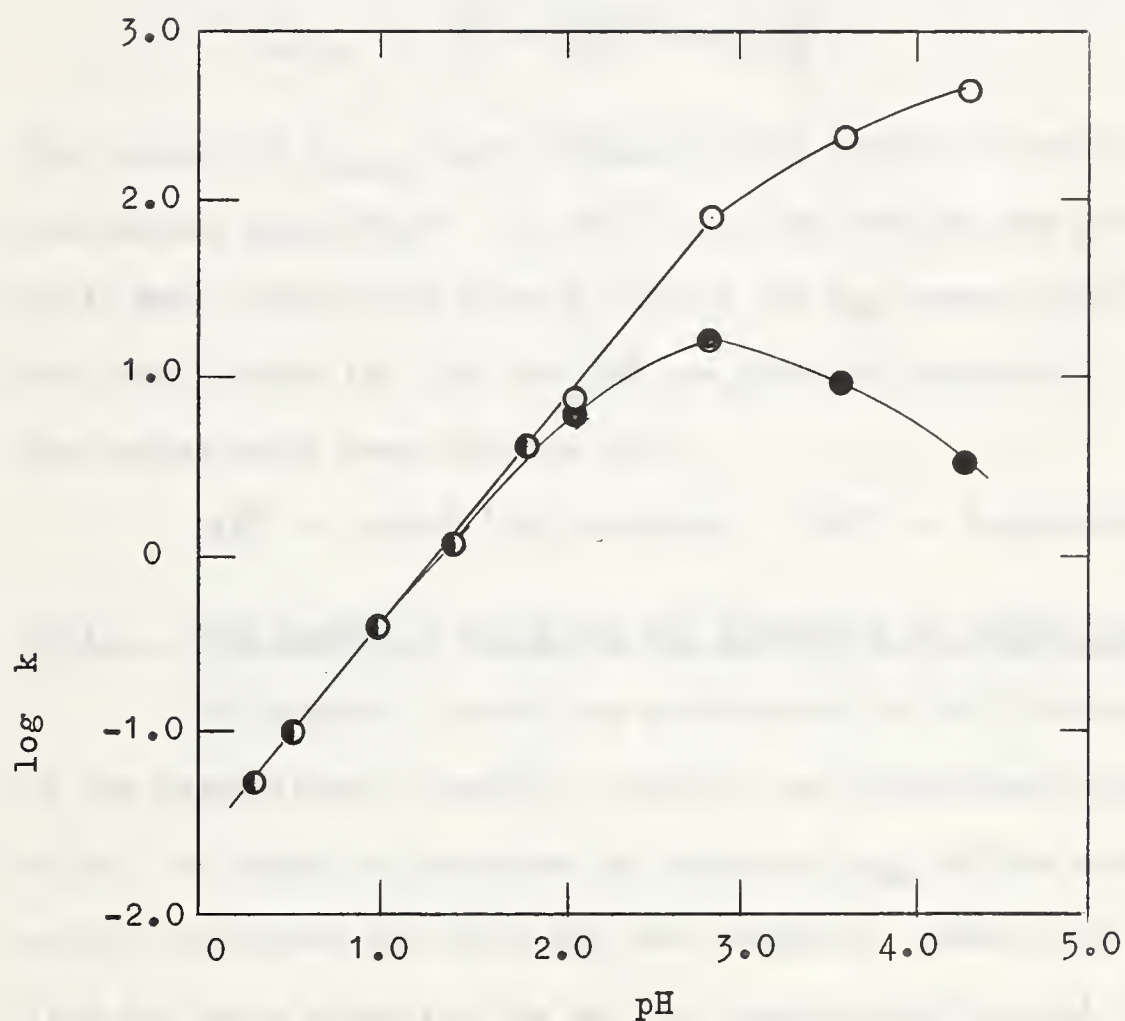


Fig. XVII The Reduction of Phenylpropionic Acid by Chromium (II)

Perchlorate in the Presence of Acetic Acid and Sodium

Acetate: Dependence of $\log k_{\text{obs}}$ and $\log k_{\text{HA}}$ on pH.

Temperature = $40.0 \pm 0.05^\circ$

(AcOH) = 1.6 mole.l^{-1}

Ionic Strength = 0.50

Legend

● $\log k_{\text{obs}}$ and $\log k_{\text{HA}}$

○ $\log k_{\text{HA}}$

● $\log k_{\text{obs}}$

(vii) THE EFFECT OF TEMPERATURE ON THE RATE

The values for ΔS^\ddagger and ΔH^\ddagger for the reduction of phenylpropionic acid were calculated from the equation derived from The Absolute Reaction Rate Theory (33) given below.

$$k_{\text{soln.}} = \frac{kT}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \cdot \exp\left(-\frac{\Delta H^\ddagger}{RT}\right)$$

The values for $k_{\text{soln.}}$ were obtained from a series of runs in the temperature range 30.0° to 50.0° , and the results are shown in Table XVI. Fig. XVIII shows a plot of $\log k_{\text{HA}}$ versus $(T^\circ\text{K})^{-1}$, and the calculations for ΔH^\ddagger and ΔS^\ddagger are shown in appendix I.

The values which were obtained are

$$\Delta S^\ddagger = -42.6 \pm 0.5 \text{ eu/mole} \quad \Delta H^\ddagger = 4.94 \text{ kcal/mole}$$

(viii) THE HAMMETT ρ VALUE FOR THE REDUCTION OF PHENYLPROPIOLIC ACIDS

The Hammett ρ value was established at 40.0° making use of the para-methoxy-, methyl-, chloro-, and bromo-phenylpropionic acids. In order to calculate the values of k_{HA} for the substituted acids, the values for their pK_a were required. These were calculated from the known value for the pK_a for phenylpropionic acid (34) and the Hammett ρ value for the dissociation of phenylpropionic acids given by Newman (27). The compounds gave a fairly good straight line when $\log (k_{\text{HA}_X}/k_{\text{HA}_H})$ was plotted versus the Hammett σ_x values for the substituents. (Fig. XIX and Table XVII). The ρ value obtained was $+0.3$. This value is consistent with the transfer of a negative entity to the organic substrate in the rate determining step. The magnitude of ρ is probably misleading, since it is likely that a pre-equilibrium exists between the organic substrate and the chromium (II) ion, forming a π -bonded complex, and such a step would be expected to have a negative ρ . The observed ρ value is probably a combination of the two.

TABLE XVI

THE REDUCTION OF PHENYLPROPIOLIC ACID BY CHROMIUM(II)
PERCHLORATE: VARIATION OF RATE COEFFICIENT WITH TEMPERATURE

(AcOH) = 1.6 mole.l⁻¹ Ionic Strength = 0.5
pH = 1.40
Temperature Controlled to $\pm 0.05^\circ$

T°C	T°K	$10^3 \times \frac{1}{T^\circ K}$	k _{obs}	k _{HA}	log k _{HA}
30.0	303.3	3.300	0.758	0.868	-0.061
35.0	308.3	3.247	0.865	0.994	-0.003
40.0	313.3	3.195	1.01	1.16	0.065
45.0	318.3	3.145	1.15	1.31	0.117
50.0	323.3	3.096	1.34	1.54	0.188

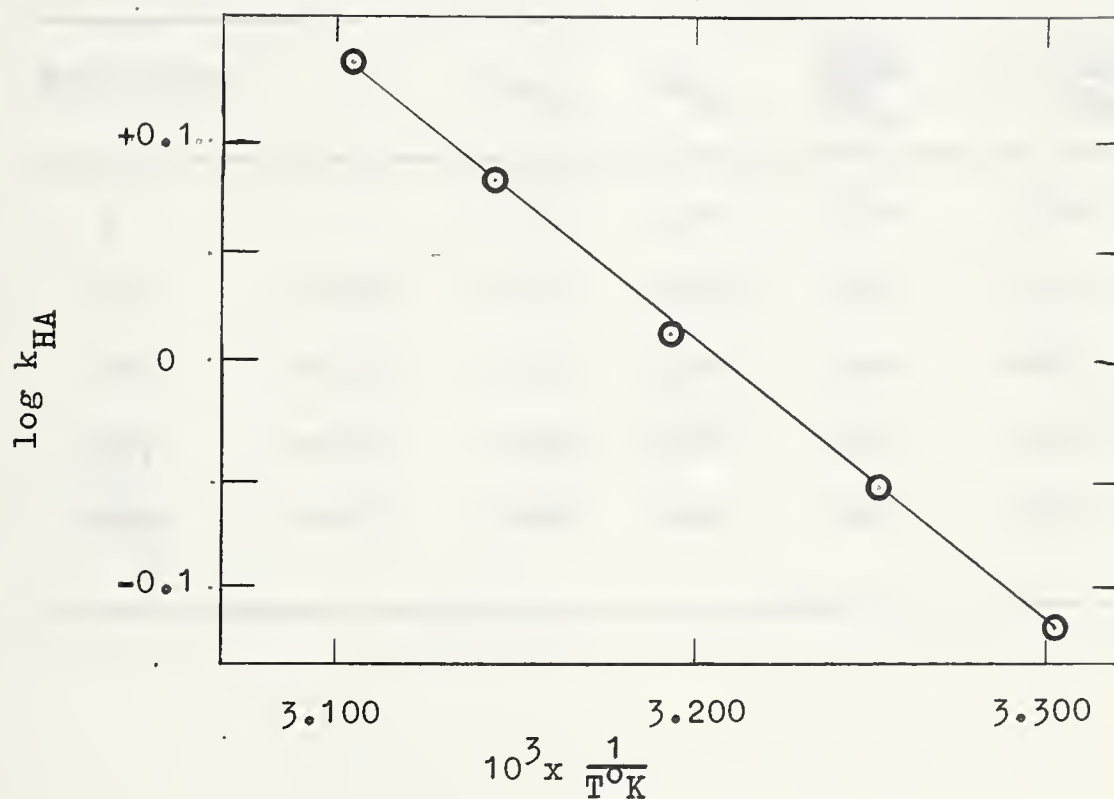


Fig. XVIII Arrhenius Plot for the Reduction of Phenylpropionic Acid by Chromium (II) Perchlorate.

(AcOH) = 1.6 mole.l⁻¹

Ionic Strength = 0.50

pH = 1.40

Slope of Line = $(-1.21 \pm 0.12) \times 10^3 \text{ degree}^{-1}$

$$\Delta H^{\ddagger} = 4.94 \pm 0.12 \text{ kcal.mole.}^{-1}$$

$$-\Delta S^{\ddagger} = 42.6 \pm 0.4 \text{ eu.mole.}^{-1}$$

TABLE XVII

REACTION COEFFICIENTS FOR THE REDUCTION OF para-SUBSTITUTED
PHENYLPROPIOLIC ACIDS BY CHROMIUM(II) PERCHLORATE

Temperature = $40.0 \pm 0.05^\circ$

Ionic Strength = 0.5

(AcOH) = 1.6 mole.l^{-1}

pH = 1.4

Substituent	σ_x	k_{obs_x}	k_{HA_x}	$\frac{k_{\text{HA}_x}}{k_{\text{HA}_0}}$	$\log \frac{k_{\text{HA}_x}}{k_{\text{HA}_0}}$
H	0	1.01	1.18	1.00	0.00
Cl	+0.23	1.13	1.24	1.20	+0.79
Br	+0.23	1.13	1.24	1.20	+0.79
CH ₃	-0.17	0.765	0.91	0.88	-0.54
OCH ₃	-0.27	0.683	0.84	0.81	-0.87

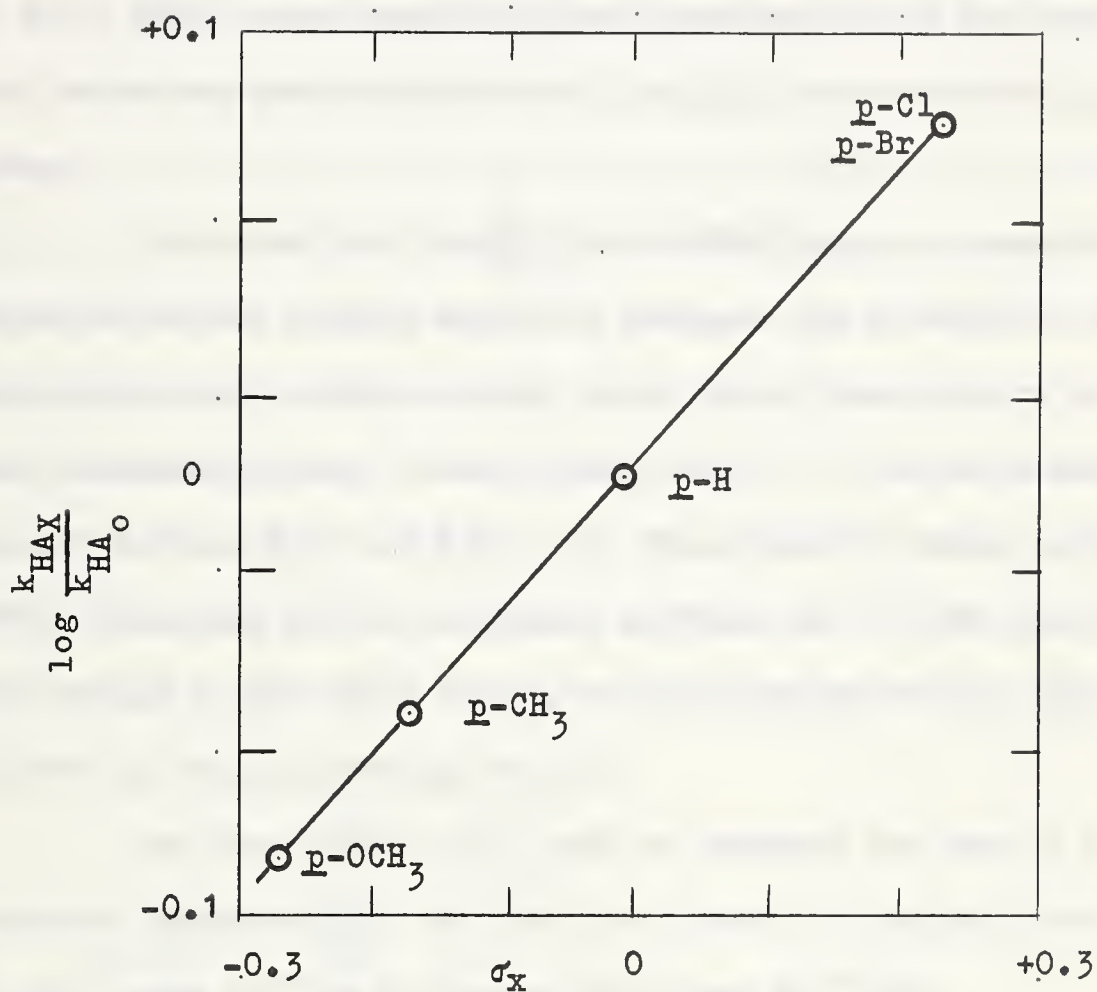


Fig. XIX. Hammett Plot for the Reduction of Substituted Phenylpropionic Acids by Chromium (II) Perchlorate

(ix) THE DEUTERIUM ISOTOPE EFFECT

Since the titrimetric method for the determination of rate coefficients would have used more D_2O than would have been economical, a spectrophotometric method was developed. Rates measured in H_2O by this method were comparable with rates measured titrimetrically, although the method does not have the potential accuracy of titrimetry. In Table XVIII rates measured spectrophotometrically are compared with rates measured titrimetrically in H_2O , and values for k_D are given.

The value, 6.6 for $\frac{k_H}{k_D}$ (Table XVIII) must be corrected for three additional effects before an estimate can be made for the deuterium isotope effect brought about by O-H bond rupture in the rate determining step. These effects are: 1) The difference in acidity between H_3O^+ and D_3O^+ ; 2) The solvation sphere isotope effect described in the historical section, and 3) The possibility of a change in the value for pK_a of phenylpropionic acid when the solvent is changed from H_2O to D_2O .

The first effect will tend to decrease the rate by a factor of approximately two when the solvent is changed from H_2O to D_2O , since D_3O^+ is a stronger acid than H_3O^+ (35).

The effect of D_2O in the solvation sphere is more difficult to assess, since there is very little information in the literature concerning this type of effect, and what information there is is not strictly applicable to the present system, for it concerns reactions between two inorganic ions, only one of which has a deuterated solvation sphere. In the reduction of phenylpropionic acid, both participating ions have a deuterated solvation sphere

and it seems likely that the isotope effect in this case would be the square of that previously observed (22,23,24), i.e. 2.25. In any case, reasonable limits for this effect can be set between 1.5 and 2.25. Consequently, in order to correct for 1) and 2) above, the observed isotope effect has to be reduced by a factor of between $2 \times 1.5 (=3)$ and $2 \times 2.25 (=4.5)$.

Martin and Butler (36) have found that the dissociation constants of weak acids are reduced by a factor of between three and four when they are dissolved in D_2O , and Högfeltdt and Bigeleisen (37) have recently shown that a similar change is observed with the conjugate acids of a series of weak bases of the Hammett indicator type. Thus it would appear from these results that in the case of phenylpropionic acid a value of ΔpK_a of about 0.5 would not be unjustified. If the values of k_{obs} in Table XVIII are corrected for the dissociation of phenylpropionic acid in H_2O and D_2O , using the assumption that $\Delta pK_a = 0.5$, the following values are obtained.

$$\begin{aligned} k_{HA} &= 0.765 \\ k_{DA} &= 0.102 \\ \text{whence } \frac{k_{HA}}{k_{DA}} &= 7.5 \end{aligned}$$

If all the appropriate correction factors are applied, a range of values for the deuterium isotope effect is obtained between 1.7 and 2.5, and this may be taken as the value of the contribution to the deuterium isotope effect from O-H bond rupture in the transition state.

This information implies that in the rate determining step, there is cleavage of a bond to hydrogen. Presumably this

occurs when a hydrogen atom or ion is transferred from a water molecule in the inner coordination sphere of one of the chromium ions to one of the carbon atoms in the triple bond. The value of $\frac{k_H}{k_D}$ suggests that the species being transferred could reasonably be a hydride ion, since Wiberg (38) has concluded that for the transfer of a hydride ion the expected isotope effect is of the order of two to four at room temperature.

The evidence for hydride ion transfer is further strengthened by the positive value for the Hammett ρ constant for the reaction, which is consistent with the transfer of a negative entity to the conjugated system in the rate determining step.

TABLE XVIII

THE REDUCTION OF PHENYLPROPIOLIC ACID BY CHROMIUM(II)
PERCHLORATE: REACTION COEFFICIENTS IN H₂O AND D₂O

Temperature = 25±0.5°
(AcOH) = 1.6 mole.l⁻¹

Ionic Strength = 0.5
pH = 1.40

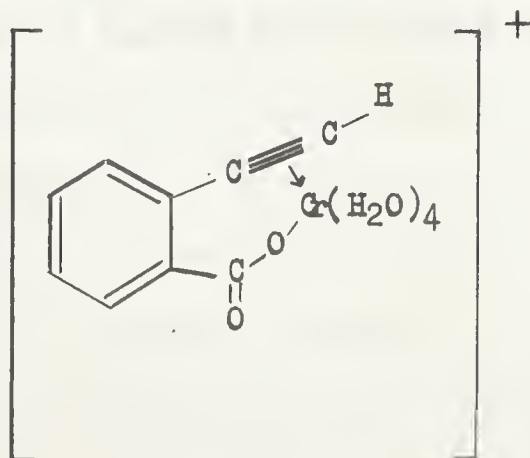
Solvent	k _{obs}	Method
H ₂ O	0.649	Titrimetric(a)
H ₂ O	0.68	Spectrophotometric
D ₂ O	0.10	"
H ₂ O	0.62	"
D ₂ O	0.098	"

$$\frac{k_H}{k_D} = 6.6$$

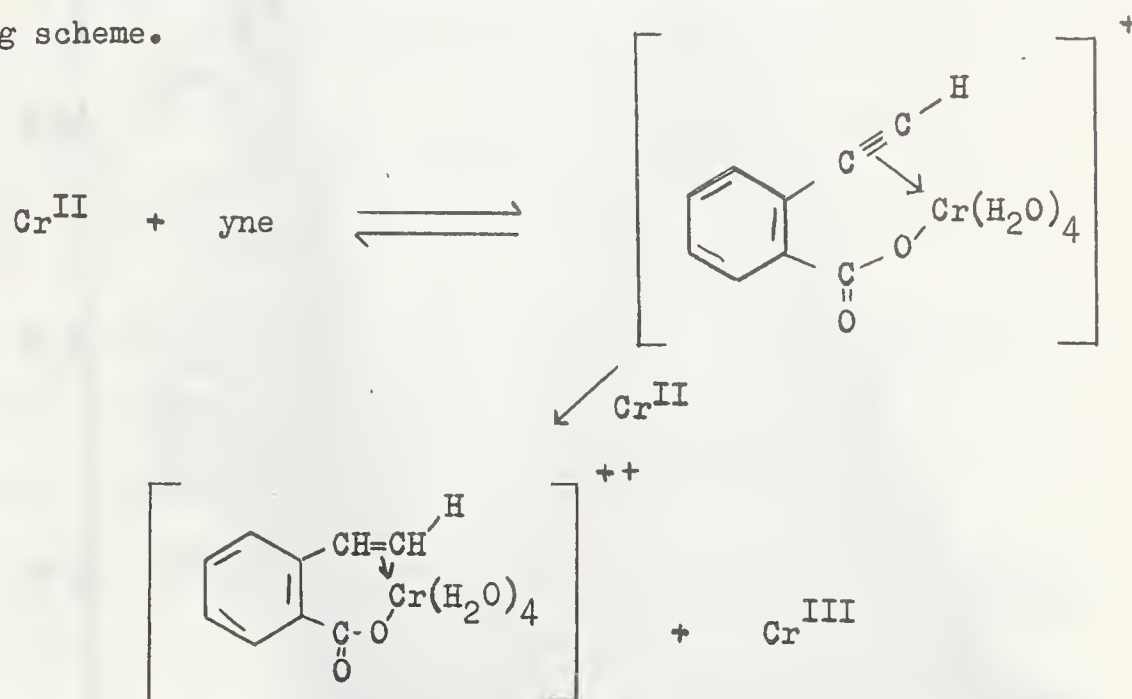
(a) By extrapolation of the line in Fig. XVIII

(x) THE REDUCTION OF *ortho*-ETHYNYLBENZOIC ACID

The reduction of *ortho*-ethynylbenzoic acid was investigated as part of a study whose object was to determine whether the organic substrate was present in the inner coordination sphere of the chromium (II) ion at any time during the reaction. Fig. XX is a reproduction of the absorption spectra of the reaction mixture obtained at different times during the reaction in the manner which is described on page 99. There are two points of interest in this figure. The first is the very rapid disappearance of the peak at 700 mμ. This peak is associated with the hexaquo chromium (II) ion, and it had completely disappeared within two minutes from the time of mixing (Curves 1, 2, 3 and 4). This cannot be taken to indicate a very rapid conversion of chromium (II) to chromium (III) however, as curve 4 exhibits no maximum in the region of 575 mμ, which is the wavelength at which chromium (III) has maximal absorption. Thus it would appear that when the reactants are mixed there is formed a stable complex which slowly decomposes to yield the products of the reaction. This complex may be a chromium (II) complex of the type depicted below, in which the *ortho*-ethynylbenzoic acid is acting as a bidentate ligand.



The second point of interest concerning Fig. XX is that there is no isobestic point, and that the absorption spectrum of the product corresponds with neither the mononuclear nor the dinuclear chromium (III) species. This implies that there are at least two different chromium (III) ions being produced in the reaction, and that at least one of them is different from the two ions whose spectra are known. These observations may be rationalised by the following scheme.



It would thus appear that the reduction of ortho-ethynylbenzoic acid gives rise to a material which is very probably an inner coordination sphere complex of chromium (III). Zeiss (39) has recently demonstrated that π complexes of alkynes can be formed in aprotic solvents.

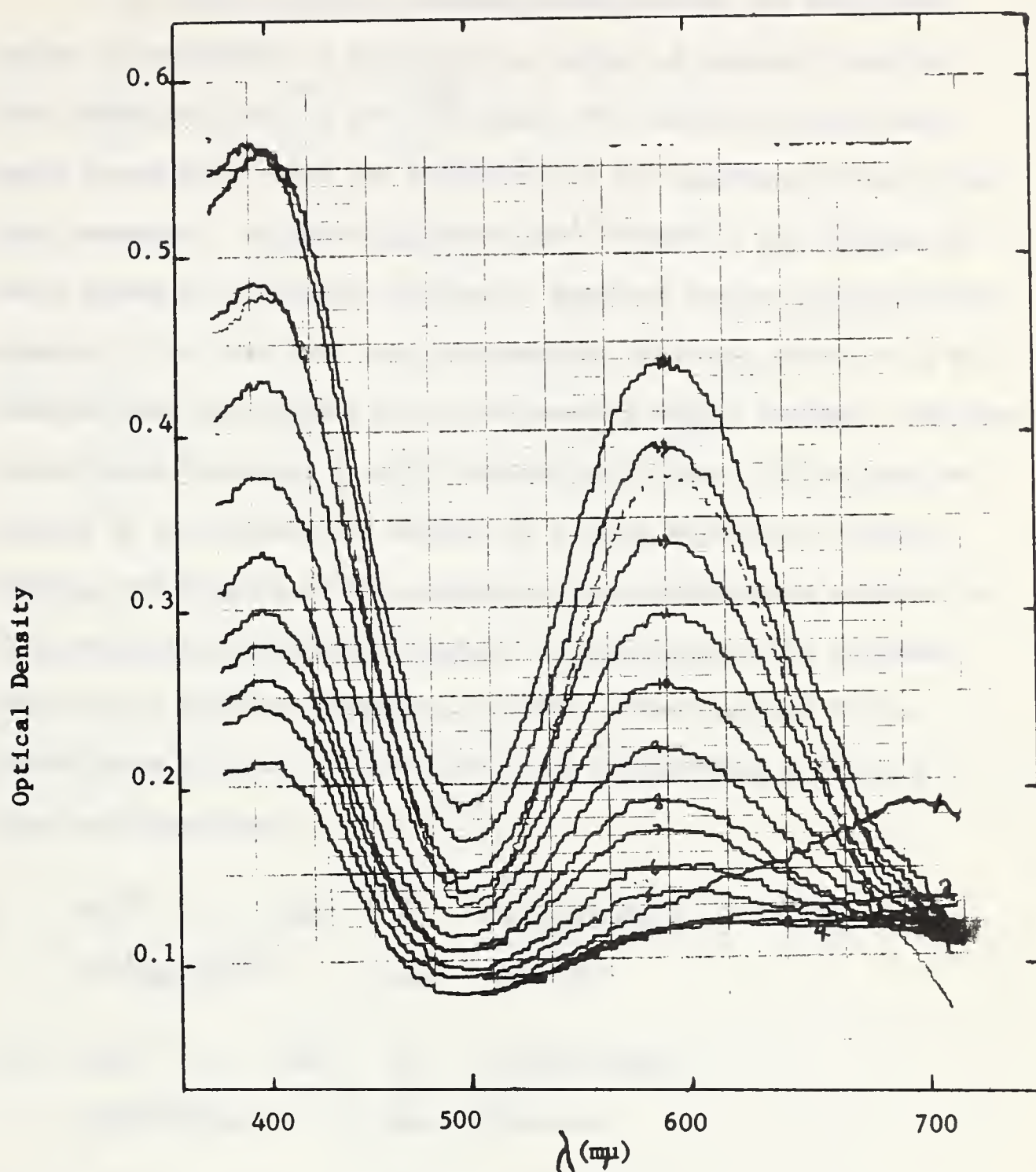


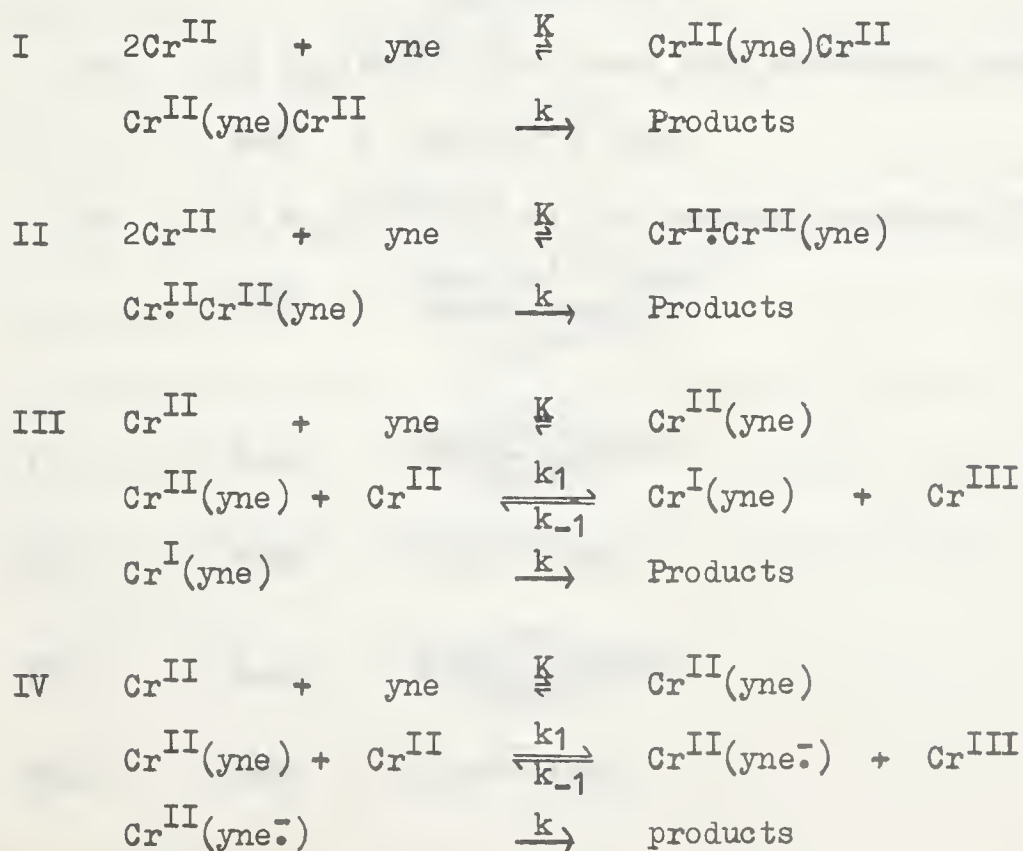
Fig XX The Reduction of ortho-ethynylbenzoic acid by Chromium (II) Perchlorate: Absorption Spectra at Different Times During the Reaction. $\text{pH} = 1.4$ Temperature = $25 \pm 0.5^\circ$.

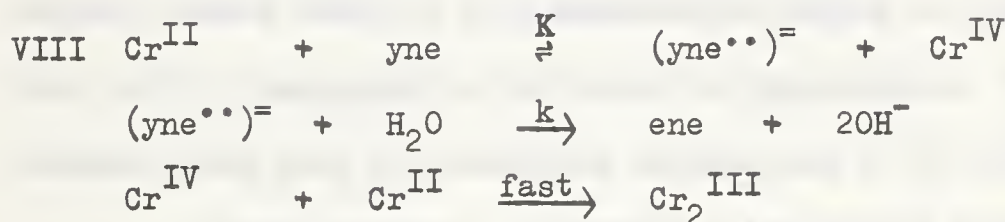
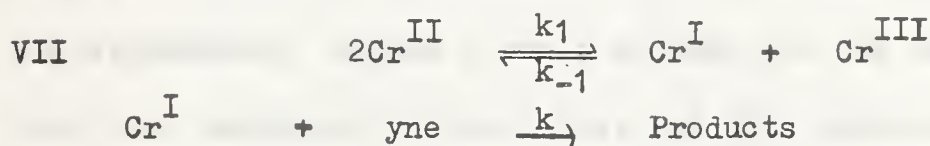
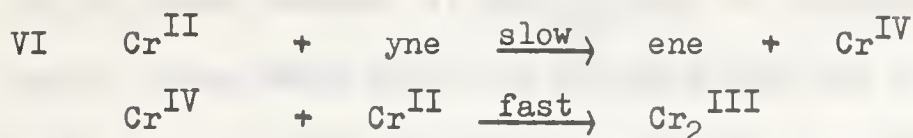
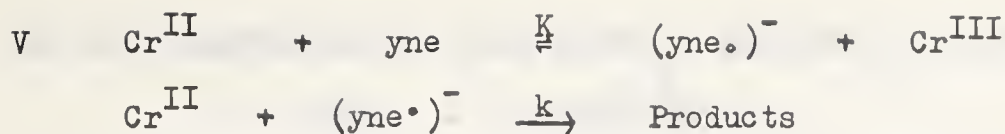
Legend

- Reaction Mixture, t_0 to t_∞
 ----- Absorption of the Dinuclear Ion

(xi) POSSIBLE MODES OF HOMOGENEOUS REDUCTION BY CHROMIUM (II) ION

In order to acquire information concerning the transition state, it is helpful to postulate the series of separate reaction steps which may lead to its formation. The possible steps which could conceivably occur are symbolized in the equations which follow this paragraph. In these equations, Cr^{II} refers to any species in which chromium is formally divalent. Positive charges and hydration spheres on the ions have been deliberately omitted, since it is not intended that each symbol should represent a unique species. The same symbol could represent a set of species which might differ from one another by the presence or absence of a water molecule or proton. However, the purpose of this section is to elucidate the sequence of steps which are kinetically feasible in the light of the evidence which has so far been presented, and the intimate nature of the participants will be discussed after any incompatible mechanisms have been discarded.





Applications of steady state approximations to the above reaction schemes lead to the following set of rate expressions.

$$\text{I and II} \quad \text{Rate} = Kk(\text{Cr}^{\text{II}})^2(\text{yne})$$

$$\text{III and IV} \quad \text{Rate} = \frac{Kk_1k(\text{Cr}^{\text{II}})^2(\text{yne})}{k_{-1}(\text{Cr}^{\text{III}}) + k}$$

a If $k_{-1}(\text{Cr}^{\text{III}}) \ll k$, then this expression reduces to

$$\text{Rate} = Kk_1(\text{Cr}^{\text{II}})^2(\text{yne})$$

b If $k_{-1}(\text{Cr}^{\text{III}}) \gg k$, the expression reduces to

$$\text{Rate} = \frac{Kk_1k(\text{Cr}^{\text{II}})^2(\text{yne})}{k_{-1}(\text{Cr}^{\text{III}})}$$

$$\text{V} \quad \text{Rate} = \frac{Kk(\text{Cr}^{\text{II}})^2(\text{yne})}{(\text{Cr}^{\text{III}})}$$

$$\text{VI} \quad \text{Rate} = k(\text{Cr}^{\text{II}})(\text{yne})$$

$$\text{VII} \quad \text{Rate} = \frac{Kk(\text{Cr}^{\text{II}})^2(\text{yne})}{(\text{Cr}^{\text{III}})}$$

$$\text{VIII} \quad \text{Rate} = k(\text{Cr}^{\text{II}})(\text{yne})$$

The rate expression has been shown in section (v) to be:

$$\text{Rate} = k_3(\text{Cr}^{\text{II}})^2(\text{yne})$$

Of the above schemes, VI and VIII may be discarded on a simple kinetic basis. From Table XII it is observed that the chromium (III) ion fails to inhibit the reaction, and thus schemes IIIb, IVb, V and VII are eliminated. Scheme V would account for the kinetics if the first step were rapid and irreversible, but this requires that the $(\text{yne}^\bullet)^-$ radical should build up in concentration during the reaction, and this sort of mechanism is difficult to rationalize. Thus the only schemes which must be considered further are I, II, IIIa and IVa.

These schemes all involve a transition state in which all three reacting species are together in the rate determining step. It would be expected that a highly ordered transition state of this type would cause the reaction to exhibit a very negative entropy of activation. Oxidation reduction reactions between two transition metal ions generally lead to ΔS^\ddagger values in the region of -20 to -40 eu/mole. (Table XIX). If the reaction under consideration in the present investigation followed one of the four paths which have been suggested for it, then it would be expected to have an even more highly ordered transition state than the reactions described above, for in this case the presence of the organic substrate is required. The results shown in Table XVI and Fig. XVIII are therefore gratifying in that they indicate a value of ΔS^\ddagger of -40.5 ± 0.5 eu/mole., which is consistent with the reaction pathways which have been postulated as schemes I to IVa.

TABLE XIX

ENTROPIES OF ACTIVATION FOR SOME
INORGANIC REDOX REACTIONS AT 25°. (40)

Reaction	ΔS^\ddagger (eu/mole)
$\text{Fe}^{+2} - \text{FeOH}^{+2}$	-18
$\text{Fe}^{+2} - \text{FeCl}^{+2}$	-24
$\text{Tl}^{+1} - \text{Tl}^{+3}$	-33
$\text{Co(en)}_3^{+2} - \text{Co(en)}_3^{+3}$	-33
$\text{Co(EDTA)}^{-2} - \text{Co(EDTA)}^{-1}$	-17

(xii) THE ARRANGEMENT OF THE REACTANTS IN THE TRANSITION STATE

Pathways I and II, and III and IV differ only in the arrangement of the transition state, and are otherwise indistinguishable. The two possible transition states may be symbolized for convenience as follows:

A: Cr-(yne)-Cr (Pathways I and III)

B: Cr-Cr-(yne) (Pathways II and IV)

If B is the correct configuration of the transition state, then the expected chromium (III) product via pathway II would be the dinuclear species which has been described by Ardon and Plane (16), since once the hydroxo bridge between the two chromium atoms has been established, it is difficult to imagine a mechanism apart from pathway IV whereby the bridge is rapidly destroyed. A way of distinguishing between A and B rather serendipitiously appeared when the reduction of N,N,N-trimethyl-3-phenyl-2-propynyl ammonium chloride was being studied. This compound was originally prepared in order to study the effects of bulky groups near the reaction sight, and also because it was a known compound and readily synthesized. It was noted first of all that it is reduced about 10^{-4} times as fast as the slowest of the other alkynes (Table XX). A more important fact was observed when the absorption spectrum of the chromium (III) product was obtained. The spectrum corresponded, not with the purple $\text{Cr}(\text{H}_2\text{O})_6^{+3}$ species, but with the green dinuclear species. This is shown in Fig. VIII, which is a reproduction of the spectra obtained at different time intervals during the reaction in the manner which is described on page 99. In this figure, the curve taken at t_{∞} has been compared with the absorption curve of both the mononuclear and the dinuclear species, and it clearly corresponds with that of the latter ion.

TABLE XX

RATES OF REDUCTION FOR DIFFERENT ACETYLENIC COMPOUNDS

Temperature = $40.0 \pm 0.05^\circ$ Ionic Strength = 0.50

pH = 4.2 (Pyridine - Perchloric Acid)

Substance	k_3
$\text{C}_6\text{H}_5\text{C}\equiv\text{C}\cdot\text{CO}_2\text{H}$	4.6×10^3 (a)
$p\text{-Me}_3\text{N}\cdot\text{C}_6\text{H}_5\text{C}\equiv\text{CH}$	1.0×10^4 (b)
$\text{C}_6\text{H}_5\text{C}\equiv\text{C}(\text{CH}_2)_2\text{NMe}_3^+$ (II)	8.9×10^2
$\text{C}_6\text{H}_5\text{C}\equiv\text{C}\cdot\text{CH}_2\text{NMe}_3^+$ (I)	3.5×10^{-1}

(a) k_{HA}

(b) Estimated by extrapolation of the line in Fig. XV

(I) Trimethyl-3-phenyl-2-propynyl ammonium salt

(II) Trimethyl-4-phenyl-3-butynyl ammonium salt



PLATE I - MOLECULAR MODEL OF N,N,N-TRIMETHYL-3-PHENYL-2-PROPYNYL
AMMONIUM ION

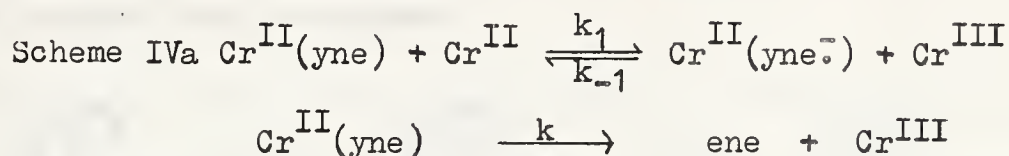
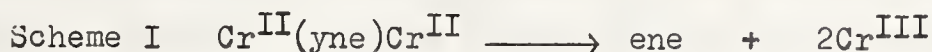
A molecular model was made of this alkyne, and a photograph of this model is shown in Plate I. The steric properties of the compound are clearly evident in the photograph, and it can be seen that the three methyl groups effectively block three sides of the triple bond, while leaving the fourth side relatively open to chemical attack. The reduction of this compound exhibited the same kinetics as did the other reductions (Table VIII), and consequently similar conclusions may be reached concerning the reaction pathway and the possible arrangements of the transition state; i.e. the reaction proceeds via one of the pathways I, II, III or IV, and the transition state has arrangement either A or B. However, the steric properties of this particular molecule are such that once one chromium (II) ion has been coordinated to the triple bond, the bond is completely blocked, and further attack has to be on the chromium (II) ion already in the complex. Hence, conformation A is highly unlikely in this case. This means that for the reduction of this highly sterically hindered alkyne, the transition state appears to have had arrangement B. It is highly significant that when B is the most likely arrangement of the transition state, the inorganic product is the green dinuclear chromium (III) ion. This carries the very strong implication that when the inorganic product is the mononuclear ion, the transition state had conformation A. Since the inorganic product has been observed to be the mononuclear ion in all cases except for the one discussed above, it would appear that the normal arrangement of the reactants in the transition state is:



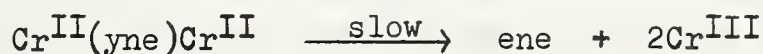
Hence mechanisms II and III may be eliminated from further discussion, since both of these require that the attack of the second chromium (II) ion is on the chromium (II) ion already in the complex, and the above considerations lead to the conclusion that the attack by the second chromium (II) ion is directly onto the triple bond, and that in the transition state, both chromium (II) ions are involved directly in some way with the triple bond.

(xiii) THE RATE DETERMINING STEP

Two possibilities still remain for the rate determining step. These may be represented by the following equations:

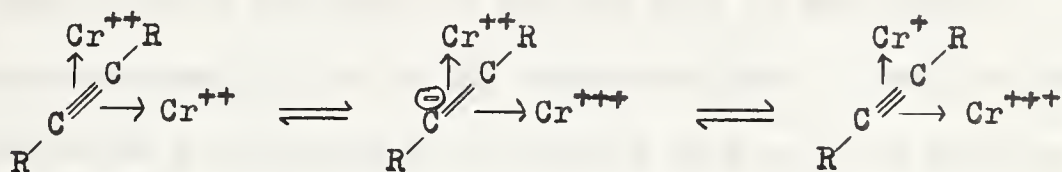


For scheme IVa, the absence of any detectable rate depression by the chromium (III) ion means either that $k_{-1}(\text{Cr}^{\text{III}})$ is much less than $k(\text{Cr}^{\text{II}}\text{yne}^-)$, or that the initially formed Cr^{III} ion does not become separate from the triple bond system before the rate determining step. The first stage in scheme IVa is the transfer of an electron from a chromium (II) ion to the triple bond, and it is difficult to imagine such a transfer taking place without prior formation of a coordinate bond between the two reacting species. This means that the only difference between schemes I and IVa is that in I the formation of the triple complex is reversible, while in IVa it may be irreversible. It is not possible in the light of the evidence which is available, to distinguish between these two possibilities, and the remainder of the discussion may be confined to considerations of possible mechanisms for the following unimolecular decomposition.



The first stage in this decomposition could be the electron transfer mentioned above. After the transfer, there are two possible fates for the electron: It can either remain in a non-bonding p-orbital on one of the carbon atoms of the triple bond, or it can be transferred before the rate determining step to the other

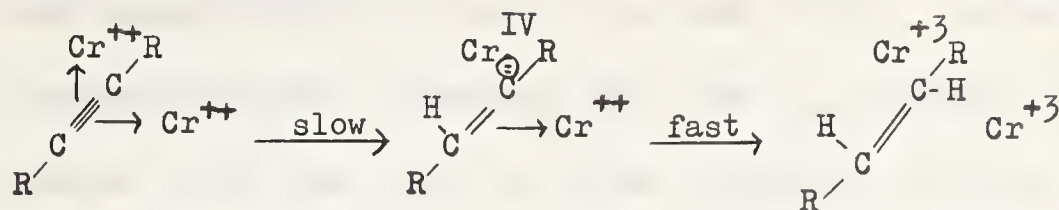
chromium atom in the complex. The latter possibility is the more attractive, since in the former case the rate determining step would be the transfer of a hydride ion to an entity which was already negatively charged. Thus the initial stages of the decomposition of the complex may be written:



For this mechanism, the species which is postulated to exist immediately prior to the rate determining step contains a monovalent chromium ion complexed to the carbon-carbon triple bond. The triple complex in the above drawing has been depicted with the two chromium ions at right angles to one another. The other arrangement, with the chromium ions directly opposite one another on either side of the bond is conceivable, although it is considered to be unlikely, for the formation of the first dative bond to chromium (II) will polarize the electrons in the triple bond, thus reducing the electron density on the side of the triple bond opposite the chromium ion, and hence the second chromium (II) ion is more likely to approach the complex at right angles to the first, where the electron density is higher. Reasonable final steps in the reaction are, in view of the observed isotope effect, a slow transfer of a hydride ion from the hydration sphere of the monovalent chromium ion to a carbon atom, followed by rapid proton abstraction from the solvent, or from the hydration sphere of the initially formed chromium (III) ion, which may still be complexed with the acetylenic system.

It is reasonable at this stage to question whether or not the hydride ion transfer could take place before the above electronic

rearrangement, thus giving a mechanism which could be written:



If this is to be the case, we can ask what is the function of the second chromium(II) ion in the triple complex? It may be simply to polarize the π -electrons of the triple bond so as to make the hydride ion transfer possible. However, it does not seem reasonable to propose that the ion performing this type of function should be exclusively the chromium (II) ion, and if the second ion were acting merely as a polarizing force, then it would be expected that any other positive ion with a labile hydration sphere could act in a similar fashion. The high rate coefficients which were observed at the start of this investigation (Table II) may have been caused by zinc ion catalysis, and although no experiments have been performed to test this hypothesis, if the reaction were indeed catalyzed by zinc, or other ligand labile ions, then the above mechanism would become more attractive. As it is however, the postulation of the intermediate formation of a chromium (IV) species cannot be regarded as an attractive hypothesis, because one would then expect the formation of at least some of the dinuclear chromium (III) ion.

The above considerations lead to the conclusion that the $\text{Cr}^{\text{I}}(\text{yne})\text{Cr}^{\text{III}}$ complex is a not unreasonable intermediate in the unimolecular decomposition under discussion. It is now pertinent to enquire whether or not the path which has been suggested for its formation is the most probable one, or if there is available a path of

lower energy which would lead to the same result. An examination of molecular models indicates that the d_{xy} orbitals of the chromium (II) ions are in close proximity with one another in the complex which has been formulated as $\text{Cr}^{\text{II}}(\text{yne})\text{Cr}^{\text{II}}$, and there is a distinct possibility of overlap between these two orbitals (See Fig. XXI). These orbitals each have the same energy, and each is capable of accepting an electron, and there seems no reason why a rapid exchange of electrons should not occur between them. It is likely that this type of electron exchange would be reversible, the odd electron tending to reside on one or other of the chromium atoms, according to the relative phases of the "breathing" vibrations of their hydration spheres. The slow step in this type of mechanism could reasonably be the transfer of a hydride ion from the hydration sphere of the chromium atom which was momentarily monovalent, followed or accompanied by the release to the oxygen of the two electrons in the chromium non-bonding d_{xy} orbital. Such a mechanism is drawn in Fig. XXII in which, for convenience, only two of the five water molecules in the hydration spheres have been shown.

The stereospecificity of the reaction is not easy to account for on a purely mechanistic basis, but it

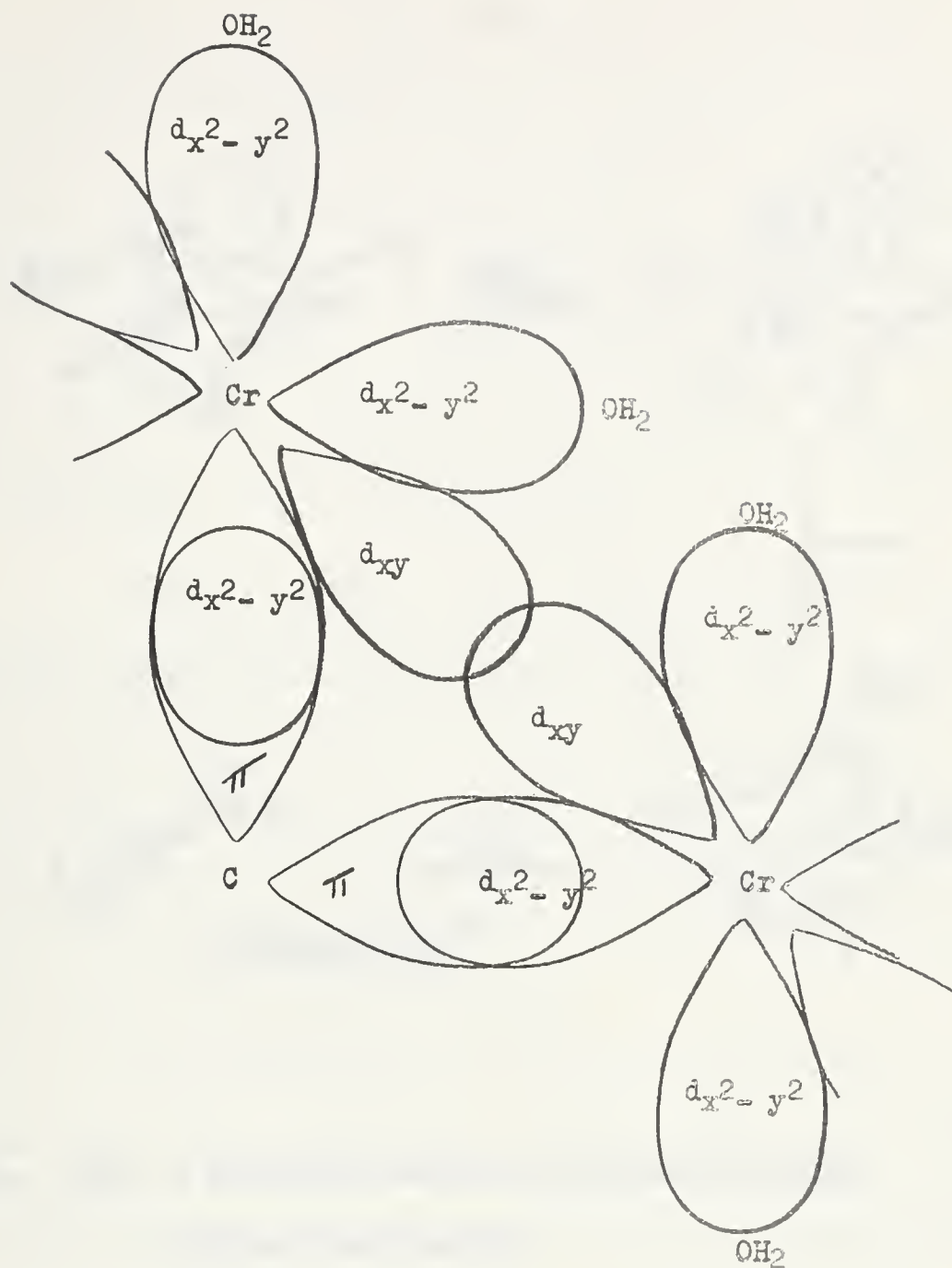


Fig. XXI Diagram Showing d_{xy} Orbital Overlap in the $\text{Cr}^{\text{II}}(\text{yne})\text{Cr}^{\text{II}}$ Complex

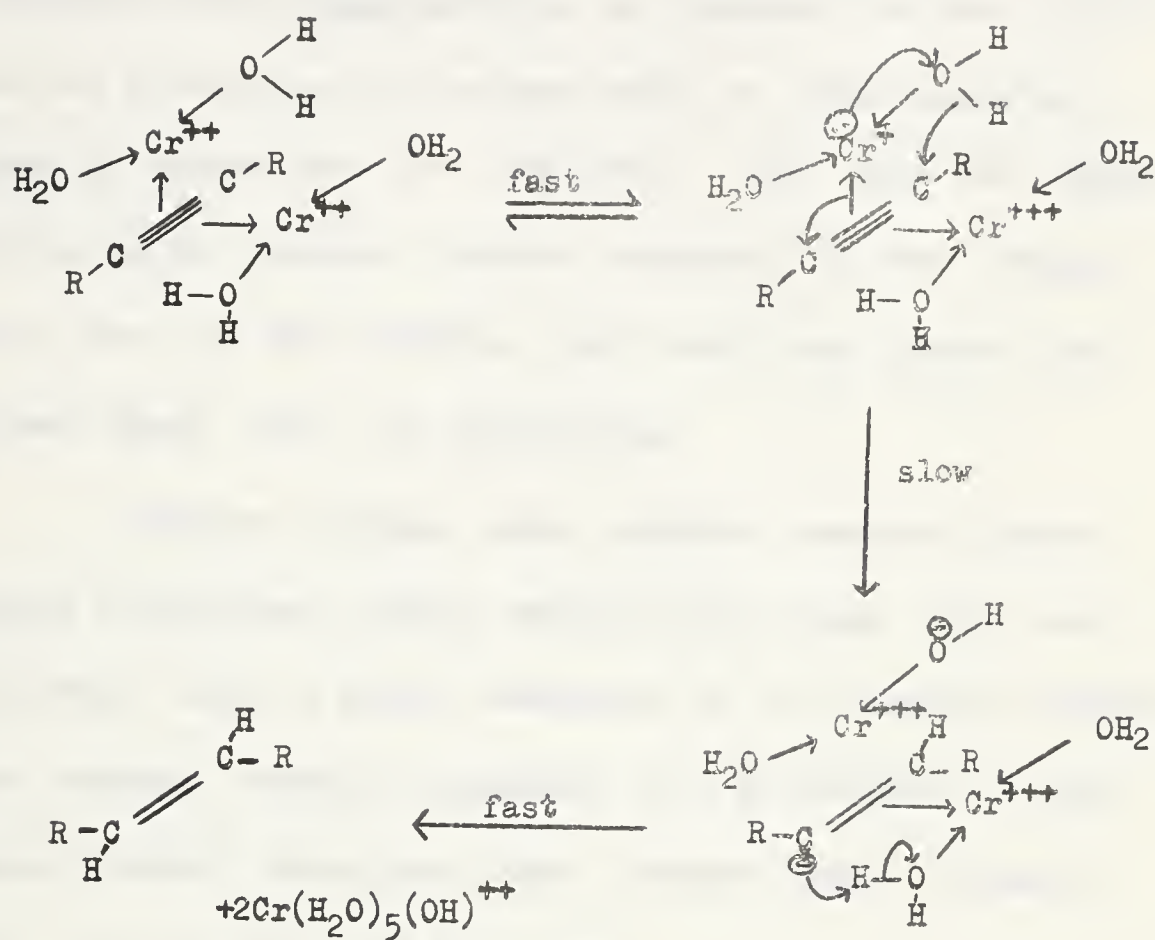


Fig. XXII A Plausible Reaction Mechanism Involving
Hydride Ion Transfer

is possible that the transfer of the hydride ion and the proton to the organic substrate molecule occur by a concerted process, and if this is the case, the stereospecifically trans-addition of hydrogen to the triple bond may be explained on the same basis as stereospecifically trans-E₂ eliminations are explained. i.e. that the trans-reaction gives a greater spatial extension of the orbitals being used in the reaction, and thus this process has a lower energy than the cis-process.

Although hydrogen atom transfer reactions which exhibit a deuterium isotope effect of less than four are relatively rare, a brief discussion of a plausible hydrogen atom transfer reaction mechanism will be included at this point, because there is no other evidence which entirely rules out this type of mechanism.

The unimolecular decomposition of the triple complex which has been formulated as Cr^{II}(yne)Cr^{II} could have as a first step the electron transfer to the organic substrate suggested on page 83;



This electron transfer could be followed by, or be concerted with the transfer of a hydrogen atom from the other chromium ion in the complex. Such a reaction mechanism is shown in Fig. XXIII. This scheme is consistent with the evidence which has been presented in this thesis, with the possible exception of the deuterium isotope effect, and thus it cannot be entirely eliminated from consideration.

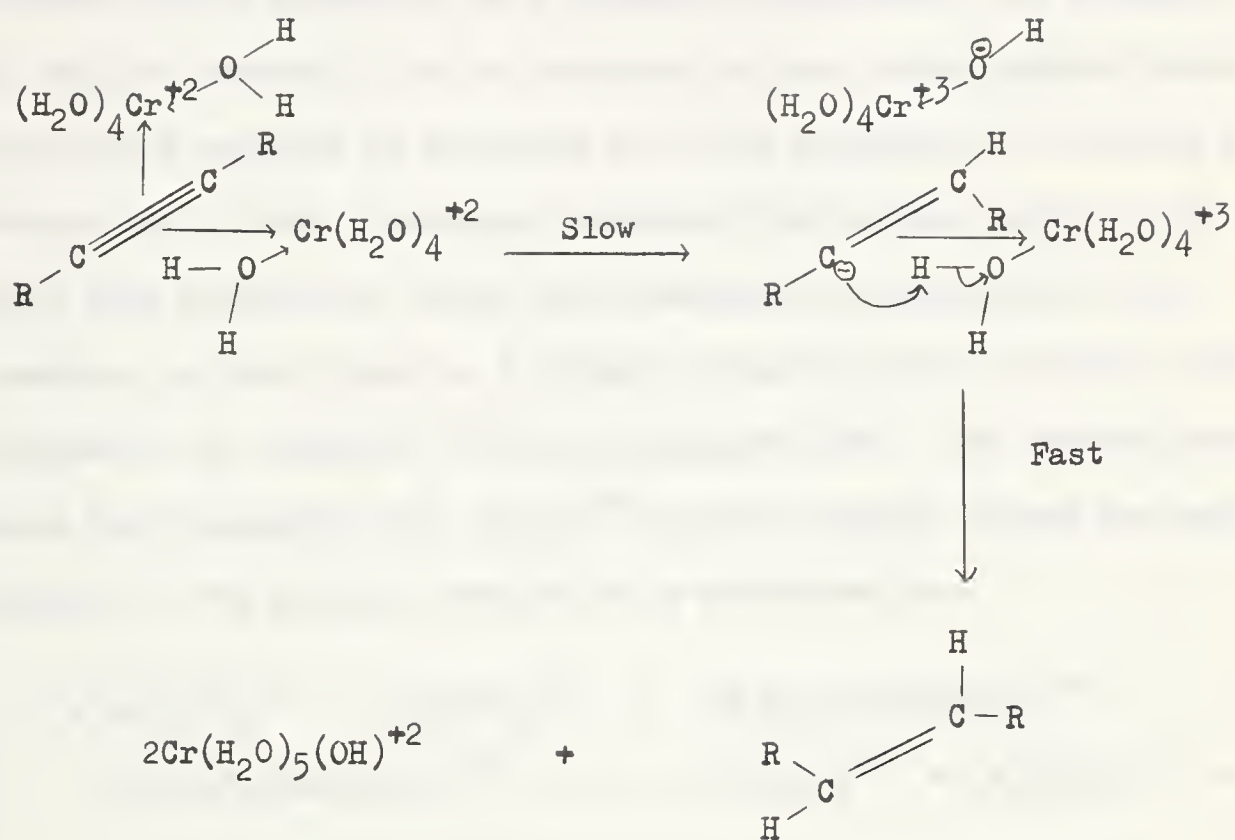
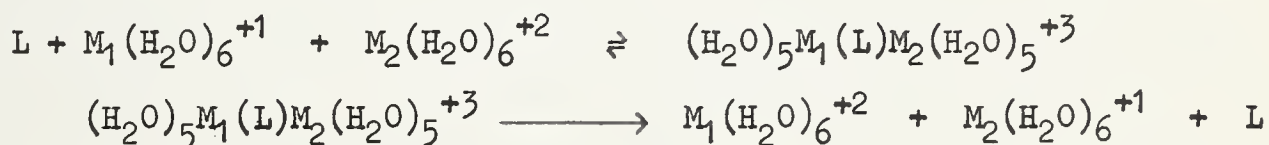


Fig. XXIII A Plausible Reaction Mechanism Involving
Hydrogen Atom Transfer

(xiv) THE ACID RATE DEPRESSION

Rate depression by acid is commonly observed in inorganic redox reactions, particularly among those which involve a bridged transition state. This phenomenon has received little attention in the literature beyond passing comments regarding its existence. However, there appears to be a plausible explanation, and although it has not received a lot of attention in this investigation beyond the effort expended in recording it, it is appropriate to include at this point a brief discussion concerning the possible cause of the acid rate depression. Since the discussion is applicable to any reaction in which there is a bridged transition state and acid rate depression is observed, it has been generalised. The reacting metals have been designated M_1^{+1} and M_2^{+2} and the bridging ligand has been called L. The general reaction to be considered is:



There are two possible cases; i.e. base catalysis, or hydronium ion depression. In both cases the explanation is similar. For base catalysis, the removal of a proton from one or more of the three complex species reduces the coulombic repulsion between M_1 and M_2 in the intermediate complex, and consequently the intermediate is rendered more stable. i.e. its formation constant will increase in the more basic solutions, and the observed rate will be greater. For hydronium ion depression the explanation is similar, except that protonation of any or all of the complex species will increase the coulombic repulsion, and cause the intermediate complex to be less

stable at the higher acidities, leading to a decrease in rate on the addition of acid to the system.

It can be seen from this argument that the order in hydroxyl ion may vary from one to three, according to the relative acid strengths of the three complex species. In the case presently under investigation, the order was approximately 1.3

EXPERIMENTAL

Melting points and boiling points are uncorrected. The ultraviolet spectra and the visible spectra were obtained using a Cary model 14M recording spectrophotometer, and the infrared spectra were obtained by Mr. R. N. Swindlehurst, using a Perkin Elmer model 21 recording spectrophotometer. The elemental analyses were carried out under the direction of Dr. F. Pascher, in the Mikroanalytisches Laboratorium, 54 Buschstrasse, Bonn, West Germany.

(i) PREPARATIONS OF THE ORGANIC SUBSTRATES AND RELATED COMPOUNDS

Phenylpropionic Acids - Substituted phenylpropionic acids were prepared according to the procedure given by Reimer (42). The substituted benzaldehydes used as starting materials were obtained from the Eastman Kodak Co., except for para-bromobenzaldehyde, which was prepared from para-bromotoluene by the method given in Organic Syntheses (43). para-methoxyphenylpropionic acid had m.p. 144°; (Newman and Merrill (27) give m.p. 144.4°); para-methylphenylpropionic acid had m.p. 150 - 151°; (Baddar et al (44) give m.p. 149 - 150°); para-chlorophenylpropionic acid had m.p. 148°; (Wilson (45) gives m.p. 147°); para-bromophenylpropionic acid had m.p. 200 - 202°; (Reimer and Tobin (46) give m.p. 200°).

N,N,N-Trimethyl-(para-ethynylphenyl) Ammonium Chloride - para-Dimethylaminophenyl acetylene was prepared by the method of Barbieri (47). The product had m.p. 57 - 59° (literature value, 56°). The methiodide was prepared by the reaction of methyl iodide with the amine in diethyl ether solution at room temperature for two hours, and had m.p. 258° (literature value, 258°)

N,N,N-Trimethyl-3-phenyl-2-propynyl Ammonium Iodide - The procedure used was that given by Mannich and Chang (30). The product had b.p. 132 - 135°(18mm.), and the methiodide had m.p. 240°. (Literature values, b.p. 137°(18mm.), and m.p. of methiodide, 240°)

N,N,N-Trimethyl-4-phenyl-3-butynyl Ammonium Iodide - N,N-Dimethyl-4-phenyl-3-butynylamine was prepared by a modification of the procedure given by Campbell et al (48). Sodium phenylacetylide was prepared by the action of sodium on phenylacetylene in diethyl ether for eight hours. The ether was allowed to evaporate under a stream of dry nitrogen, and replaced by liquid ammonia. One half of an equivalent of N,N-dimethyl-β-aminoethyl bromide (49) was slowly added to the solution of sodium phenylacetylide, and the mixture stirred for two hours. Diethyl ether was then added and the mixture allowed to stand overnight, during which time the ammonia evaporated. The ether solution of the product was filtered to remove sodium bromide, and then extracted with hydrochloric acid. The acid extract was made alkaline, and an oily layer of the desired amine separated. The amine was dissolved in ether and the solution dried over magnesium. After the drying agent had been removed by filtration, an excess of methyl iodide was added. The required quaternary ammonium salt slowly separated overnight. It was crystallized from acetone to a constant m.p. of 204°.

Anal. Calcd. for $C_{13}H_{18}NI$: C, 49.52; H, 5.71; N, 4.4.; I, 40.32

Found: C, 49.03; H, 5.78; N, 4.25; I, 37.30.

The compound had a peak in the infrared at 2220 cm^{-1} ($-C\equiv C-$), and at 1740 cm^{-1} (CO_2H).

ortho-Ethynyl benzoic acid - cis-ortho-cyanocinnamic acid, (86g.), prepared by the method of Davies and Poole (50), was treated with an equivalent amount of bromine in boiling carbon tetrachloride solution. The α - β -dibromo-ortho-cyanocinnamic acid so produced was isolated by evaporating the solvent on a steam bath. Yield 150g. (90%). The crude dibromo acid (10g.) was dissolved in 55 ml. 30% potassium hydroxide (10 equivalents) and the solution was refluxed until ammonia ceased to be evolved (about eight hours). The dark coloured solution was acidified and extracted with ether. The ether extract was dried over sodium sulphate, and upon evaporation of the solvent there was obtained a white acidic solid which was very soluble in water. It had absorption peaks in the infrared at 3300 cm^{-1} ($-\text{C}\equiv\text{C}-\text{H}$), at 2220 cm^{-1} ($-\text{C}\equiv\text{C}-$), and at 1720 cm^{-1} (CO_2H). After four recrystallisations from benzene, it had constant m.p. 138° . Yield, 1.4g. (=25%).

Anal. Calcd. for $\text{C}_9\text{H}_6\text{O}_2$: C, 73.98; H, 4.11: Found: C, 74.05; H, 4.01.

N,N,N-Trimethyl-3-phenyl-2-propenyl Ammonium Iodide - cis-N,N-Dimethyl-3-phenyl-2-propenylamine was prepared by the reduction of N,N-dimethyl-3-phenyl-2-propynylamine by hydrogen, using palladium on charcoal as catalyst, as described by Mannich and Chang (30). The hydrochloride had m.p. $146 - 147^\circ$. Literature value (30) 147° . trans-N,N-Dimethyl-3-phenyl-2-propenylamine was prepared according to the procedure given by Bunnett et al (51), and had b.p. $116 - 119^\circ$ (20mm.) Literature value (51), $125 - 132^\circ$ (25mm.). The hydrochloride had m.p. $189 - 190^\circ$. Literature value (52), 191° . The free bases were isolated, and their methiodides prepared in the usual manner. The cis-methiodide had m.p. $166 - 167^\circ$, and the trans-methiodide had m.p. $199 - 200^\circ$.

Anal. Calcd. for $\text{C}_{12}\text{H}_{18}\text{NI}$: I, 41.91: Found: cis- : I, 41.87: trans- : I, 41.85

(ii) THE EFFECT OF pH ON THE ABSORPTION SPECTRA OF
SOLUTIONS OF CHROMIUM (II) AND CHROMIUM (III) SALTS

Chromium (II) Perchlorate - Solutions of chromium (II) salts are very susceptible to atmospheric oxidation, and all manipulations involving such solutions had to be performed in closed apparatus under a nitrogen atmosphere. Chromium (II) perchlorate solutions were prepared by dissolving freshly precipitated chromium (II) acetate in perchloric acid. The chromium (II) acetate was prepared by reducing chromium (III) chloride with zinc and hydrochloric acid and mixing the resulting solution with concentrated sodium acetate.

The apparatus used to obtain the ultraviolet spectra of solutions of chromium (II) salts is shown in Fig. XXIV. The apparatus was set up as shown in Fig XXIVA and flushed with nitrogen. A solution of sodium acetate was placed in compartment B and a stream of nitrogen passed through it, and at the same time a solution of chromium (II) chloride was prepared in A as described above (0.5g. chromium (III) chloride, 0.5g. zinc and 3ml. hydrochloric acid). When the reduction was complete, the apparatus was tilted so that the chromium (II) chloride solution flowed into B, producing a red precipitate of chromium (II) acetate. A was then replaced by A' as shown in Fig XXIVB, and the apparatus was again flushed with nitrogen. It was then tilted so that the suspension of chromium (II) acetate flowed into A'. Nitrogen pressure in the apparatus was then increased and stopcock 3 was opened, thus forcing the mother liquors out through the sintered glass disc. The precipitate was washed free from soluble sodium and zinc salts by placing successive 25ml portions of water in B, deoxygenating, transferring to A' and forcing out through stopcock 3 as described above; and dried by washing with ethanol and then ether and then blowing a stream of nitrogen through the apparatus for five minutes. Stopcock 3 was then closed and 25ml. 0.4N perchloric acid was placed in B, deoxygenated

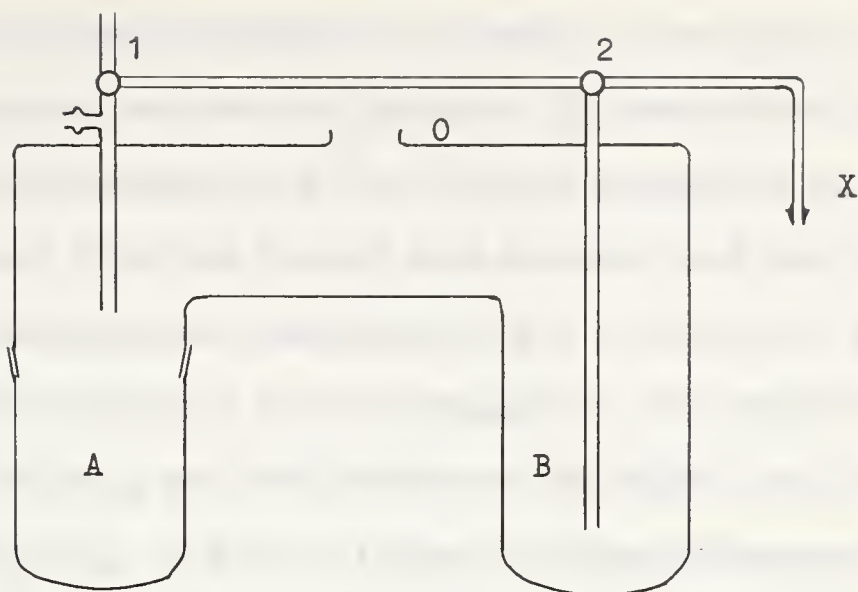


Fig. XXIVA

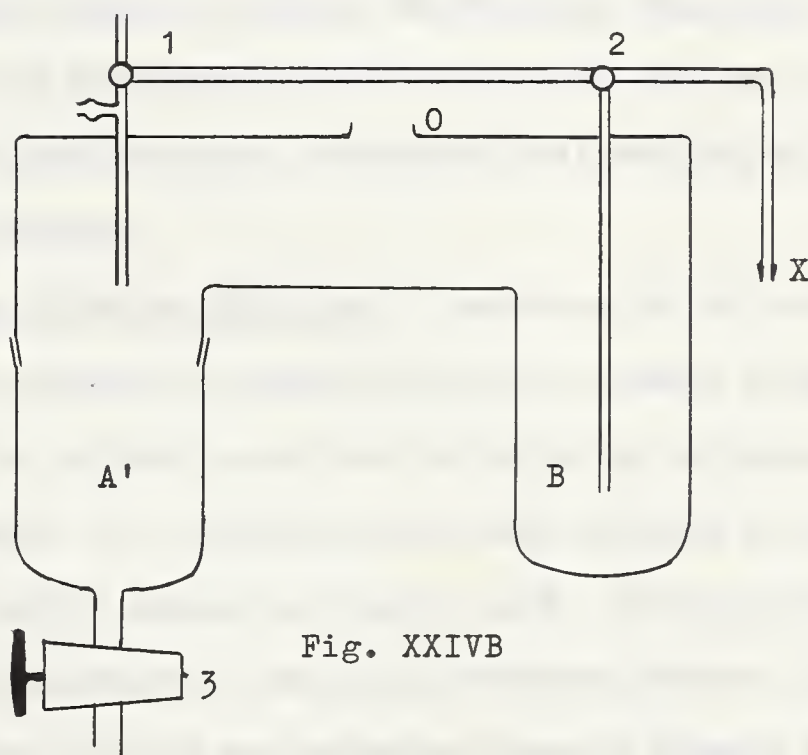


Fig. XXIVB

Fig. XXIV. Apparatus for Obtaining the Spectra of Air Sensitive
Materials

and then by tilting the apparatus was made to flow into A'. The chromium acetate dissolved, and the blue chromium (II) perchlorate solution so produced was transferred to B. A' was then replaced by A, which had been previously dried and flushed with nitrogen, and the chromium (II) perchlorate solution was transferred to A. A solution of a suitable buffer was then placed in B and deoxygenated. The chromium (II) perchlorate solution was then mixed with the buffer, and the resultant solution kept in B. A 5cm. cell from the spectrophotometer was then fitted to the male standard taper joint at X, and evacuated through the nitrogen inlet. Stopcock 1 was then closed, and 2 was turned so that the solution in B was sucked into the cell, which was then rapidly disconnected, stoppered and placed in the spectrophotometer. The total chromium content of the solution was determined using the potassium persulphate procedure described by Vogel (53). Figs. I and II show the absorption curves obtained in this way in the pH range 0.3 - 4.5 in both pyridine - perchloric acid and sodium acetate - acetic acid buffers.

The Dinuclear Chromium (III) Ion - A solution of the perchlorate of this ion was prepared by dissolving purple chromium (II) perchlorate hexahydrate in perchloric acid and allowing the solution to run through a Jones reductor into solutions which were buffered at various pH values with sodium acetate and acetic acid. The resulting solutions were then air oxidised to the green dinuclear chromium (III) perchlorate. The pH of each solution was determined using a Beckman Zeromatic pH meter, and the total chromium content was determined using the persulphate method referred to above. The absorption spectra which were obtained are shown in Fig. III.

(iii) THE ABSORPTION SPECTRA OF THE CHROMIUM (III) PRODUCTS

Several runs were performed in the spectrophotometer cell in order to follow the changes which occur in the absorption spectrum of the reaction mixture during the reduction. The apparatus shown in Fig. XXII was used, and the procedure was similar to that which was used to obtain the spectra of chromium (II) perchlorate solutions, with the following modification: after the chromium (II) perchlorate had been prepared and placed in compartment A, a solution of known concentration of phenylpropionic acid or other substrate in a suitable buffer was placed in B. The two solutions were not mixed until after the ultraviolet absorption cell had been evacuated, i.e. immediately before filling the cell. In this way it was possible to begin recording the spectrum of the reaction mixture within 25 seconds of the time of mixing, which was generally less than the time taken for one percent of the reaction to have occurred. The spectrum of the mixture was recorded at suitable intervals during the reaction, each curve being superimposed on the ones which had preceded it. Some of the spectra which were obtained are shown in Figs. V - XIX.

(iv) THE PREPARATION OF CHROMIUM (II) PERCHLORATE

The preparation was carried out in the apparatus shown in Fig. XXV. A and B are 2 l. three necked flasks, D and E are 1 l. three necked flasks, and C is a 1.l. standard taper three necked flask to the bottom of which had been sealed a coarse sintered glass 75mm. funnel and stopcock as shown. All nitrogen exits were capable of being closed by screw clamps. The nitrogen exit from C was connected to a manometer in order to follow pressure changes inside the flask.

Before the preparation was started the entire apparatus was evacuated through stopcock 11, and then filled with nitrogen through stopcock 1 several times to ensure complete removal of oxygen from the system. 1600ml. concentrated sodium acetate solution and a magnetic stirring bar were placed in flask B; flask D was filled with water which was maintained at 0° by means of an ice bath, and flask E was filled with 1N. perchloric acid. All of these solutions were deoxygenated by bubbling nitrogen through them for fifteen minutes before starting the preparation.

A solution of chromium (II) chloride was prepared in A by reducing chromium (III) chloride (50g.) with zinc (50g.) and hydrochloric acid (120ml. added over a period of fifteen minutes). When all the acid had been added, the nitrogen exit from A was closed, and stopcock 7 opened. The pressure of hydrogen being generated in A forced the chromium (II) chloride solution into B, where a red precipitate of chromium (II) acetate formed. The glass wool plug prevented any small pieces of zinc from being carried over. When all the chromium (II) chloride had been transferred to B, stopcock 7 was closed, and kept closed throughout the rest of the preparation.

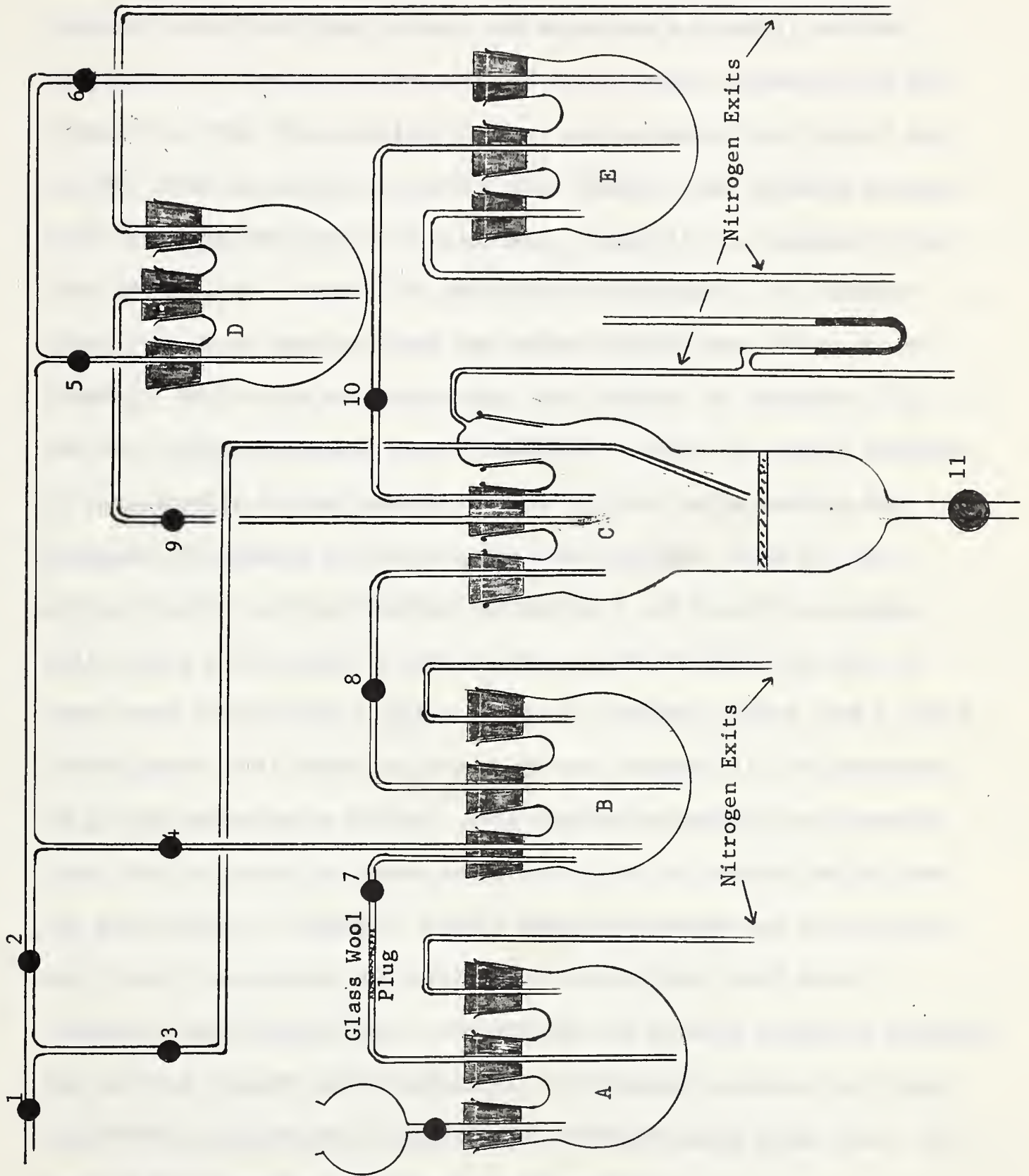


Fig. XXV Apparatus For The Preparation of Chromium (II) Perchlorate

To ensure complete precipitation of the chromium (II) acetate in B, the flask was surrounded with an ice - salt bath for one hour. At the end of this time, the magnetic stirrer in B was started, the nitrogen exit from B was closed, and stopcocks 4,8 and 11 and the nitrogen exit from C were opened; and the nitrogen pressure in B was adjusted so that the chromium (II) acetate suspension was forced into C. The stirring served to prevent the transfer tube becoming clogged with large agglomerates of precipitate. When all the suspension had been transferred, stopcock 11 was connected through a 2 l. büchner flask to a water aspirator and the mother liquors were drawn out of flask C. While this was being done, the pressure of nitrogen in C was kept slightly greater than atmospheric, either by closing stopcock 11 occasionally if the pressure became too low, or by opening the nitrogen exit from C if the pressure rose too high. When all the mother liquors had been removed, stopcocks 4 and 8 and the nitrogen exit from D were closed, 6 and 10 were opened and about 100 ml. of water were forced into C. After 6 and 10 had been closed, and 4 and 8 opened again, this water was drawn through stopcock 11, the pressure in C being adjusted as before. This washing procedure was repeated four times in order to ensure complete removal of soluble salts from the precipitate. Stopcocks 5 and 9 were then opened and the nitrogen exit from E was closed, thus forcing the perchloric acid into C. Stopcock 2 was then closed, 3 was opened, and a rapid stream of nitrogen was bubbled through the chromium (II) perchlorate solution in C while the rubber stoppers were replaced with standard taper glass ones. The rest of the apparatus could then be dismantled.

(v) KINETIC RUNS

Titrimetric - The apparatus is shown in Fig, XXVI. A measured amount of chromium (II) perchlorate could be transferred via the burette B to the reaction vessel V from the resevoir C, which contained the solution prepared by the method described in the previous section. A solution of organic substrate could be placed in the funnel F, deoxygenated and then added to the standardized chromium (II) perchlorate solution in V. Samples of the reaction mixture could be withdrawn at intervals by use of the sampler S, and these aliquots were quenched with excess ferric sulphate, and the ferrous sulphate so produced was titrated with standard potassium dichromate. The reaction vessel V was immersed in a constant temperature bath, and water from this bath was pumped through the jackets on F and S.

Before the apparatus was assembled, a known volume of the appropriate buffer solution was placed in V, together with sufficient sodium perchlorate to bring the ionic strength up to the desired value. A wieghed amount of organic substrate was dissolved in 50ml. of either glacial acetic acid or 10% aqueous pyridine, depending on the buffer system in use, and placed in F. The stopcocks were then adjusted so the S, V and B could be evacuated without affecting F or C. When the pressure in the system had fallen to about 20mm., stopcock 4 was closed to the vacuum, and 1 was turned so as to admit nitrogen to the evacuated parts of the system. This was repeated four time to ensure complete removal of oxygen. Stopcock 3 was then turned so that it connected only 2 and 4, 6 was opened and nitrogen was bubbled through the solution in V for fifteen minutes to remove dissolved oxygen. Stopcock 3 was then returned to it former position, and 1 was turned so that it admitted nitrogen only to C. The nitrogen exit from C was closed, and the nitrogen pressure in C forced chromium (II) perchlorate into B through stopcock 5. When the burette had been filled in this

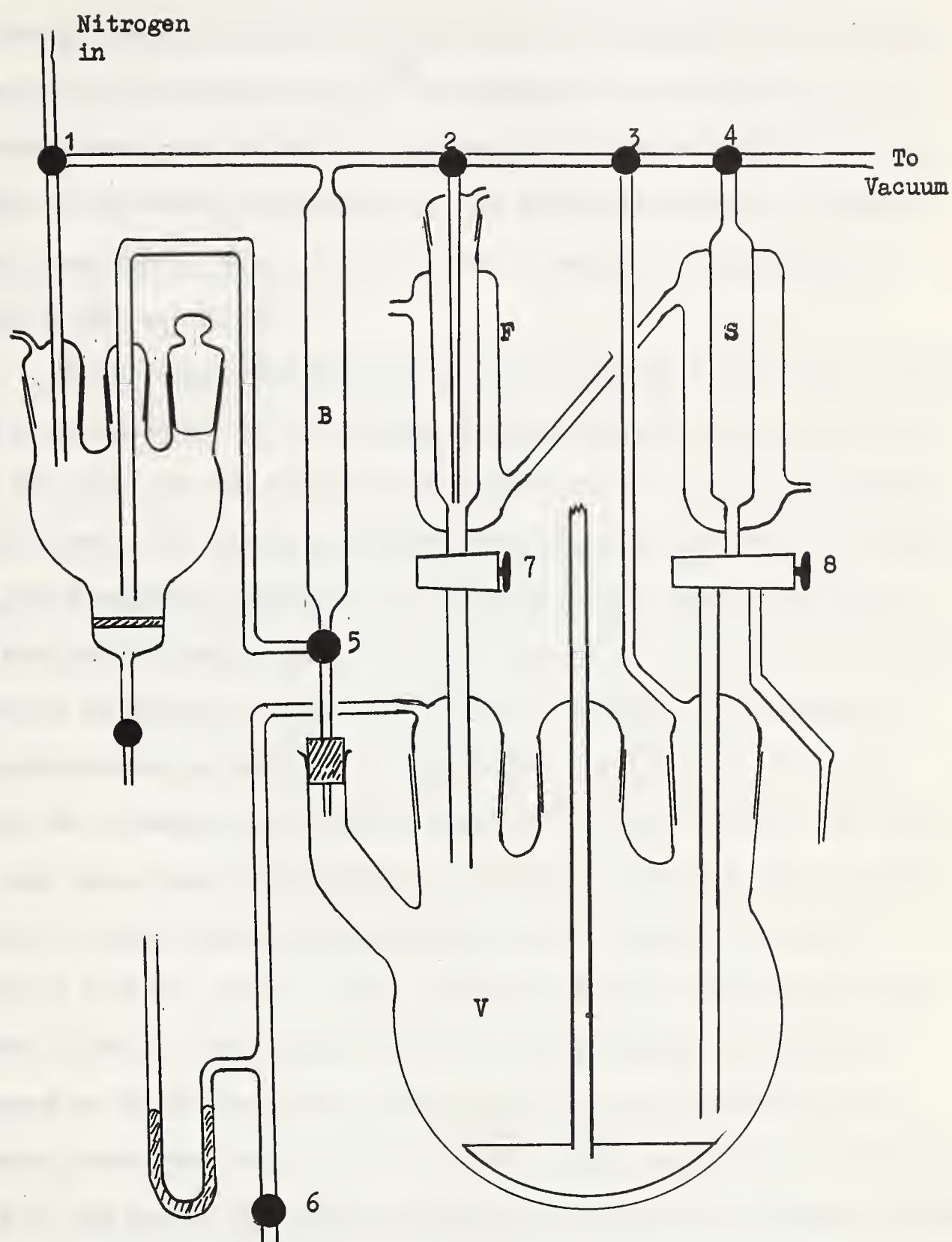


Fig. XXVI Apparatus For Titrimetric Runs

manner, stopcock 1 was turned so that it admitted nitrogen only to B and V, and 5 was turned so as to allow the chromium (II) perchlorate solution in B to flow into V. The solutions in the funnel F and the flask V were then allowed to equilibrate with the water bath for one hour. In a separate experiment, it was found that 1500 ml. of water in V took about forty minutes to come to temperature equilibrium with a bath set at 45°.

While temperature equilibrium was being established, the solution in F was deoxygenated by bubbling nitrogen through it via stopcock 2. At the same time the chromium (II) concentration in V was determined as follows. The vacuum was disconnected from the open end of stopcock 4, which was then connected to a rubber hose the other end of which dipped into the water bath. This hose served as a nitrogen exit during the run as stopcock 6 had to be closed for sampling. The sampling procedure was as follows: stopcock 3 was turned so as to connect only the nitrogen inlet with V, and with 5, 6 and 7 closed, and with 4 open three ways, the pressure of nitrogen in V forced the solution into the sampler, which had previously been calibrated to deliver 48.20 ± 0.05 ml. at 40°. When the sampler had been filled up to the mark, stopcock 8 was closed, and 3 was fully opened. 8 was then opened on the delivery side, and the solution was delivered into a beaker containing about 50 ml. of 0.01M. ferric sulphate. The delivery tip of the sampler was below the surface of the ferric sulphate solution, and the air above the solution had been replaced with a blanket of nitrogen by bubbling nitrogen through the sampler into the ferric sulphate for at least five minutes before sampling. Addition of chromium (II) to the ferric sulphate produced an equivalent amount

of ferrous sulphate, and this was titrated against standard potassium dichromate, using barium diphenylamine sulphonate as indicator.

When temperature equilibrium had been established, and the chromium (II) concentration in V was known, the nitrogen exit from F was closed, stopcock 7 was opened and the run begun.

Spectrophotometric- Runs were performed using the apparatus shown in Fig. XXIV. The procedure was exactly similar to that which has already been described for obtaining the spectrum of the product at different time intervals, except that for a kinetic run the change in optical density was observed at 575 $m\mu$ only. At this wave-length the difference in O.D. between chromium (II) and chromium (III) is maximal, and consequently the greatest accuracy could be obtained.

Rates were calculated as follows:

$$\begin{aligned}
 \% \text{ of Cr}^{\text{II}} \text{ used} &= \frac{D - D_o}{D_{\infty} - D_o} \\
 &= \alpha \\
 (\text{Cr}^{\text{II}})_t &= (1 - \alpha)(\text{Cr}^{\text{II}})_o \\
 &= 2(a-x) \\
 (\text{yne})_t &= (\text{yne})_o - \frac{1}{2}(\text{Cr}^{\text{II}})_t \\
 &= (b-x) \\
 4kt &= \int \frac{dx}{(a-x)^2(b-x)}
 \end{aligned}$$

Rate coefficients obtained in this way were comparable with coefficients obtained titrimetrically, as shown in Table XVIII.

(vi) THE PREPARATION OF DEUTEROPERCHLORIC ACID

Deuteroperchloric acid was prepared by the reaction between deuterium chloride and an equivalent amount of silver perchlorate dissolved in D_2O . The deuterium chloride was generated by adding sodium chloride to a solution of sulphur trioxide in D_2O .

The apparatus shown in Fig. XXVII was assembled, with the exception of bulb C, and the entire assembly was pumped out at 100° for twenty minutes to remove last traces of water. Bulb A contained exactly 2.3400g. sodium chloride which had been previously dried to constant weight at 100° . After dry air had been admitted to the system through stopcock 1, bulb C was sealed on, and in trap T was placed a solution of 8.2960g silver perchlorate in about 50ml. D_2O . Bulb C contained approximately 8g. sulphur trioxide which had been purified by repeated vacuum distillation at room temperature, the final distillation being into C. Three ml. D_2O was added to bulb B through the standard taper joint at X, and cooled to 0° in an ice bath. B was then evacuated through stopcock 1, and then stopcocks 1 and 2 were turned so that the sulphur trioxide in C distilled into B. Stopcock 2 was then turned so as to isolate C from the rest of the apparatus and dry air was admitted to B via stopcock 1. the contents of B were then allowed to warm to room temperature, when the sulphur trioxide dissolved to yield a solution of D_2SO_4 . An ice - salt freezing bath was then placed round the two U-traps, T was immersed in an ice bath, and bulb D was evacuated through stopcock 1. Stopcock 1 was then turned to connect B and D, and A was rotated so the sodium chloride fell into the D_2SO_4 solution. The entire apparatus was then allowed to stand for three hours so that all the DCl so produced would be absorbed by the solution in T. Bulb D was then rotated so that the suspension of silver chloride in deuteroperchloric acid flowed onto the sintered glass disc, and dry air was admitted through stopcock 1. Since the

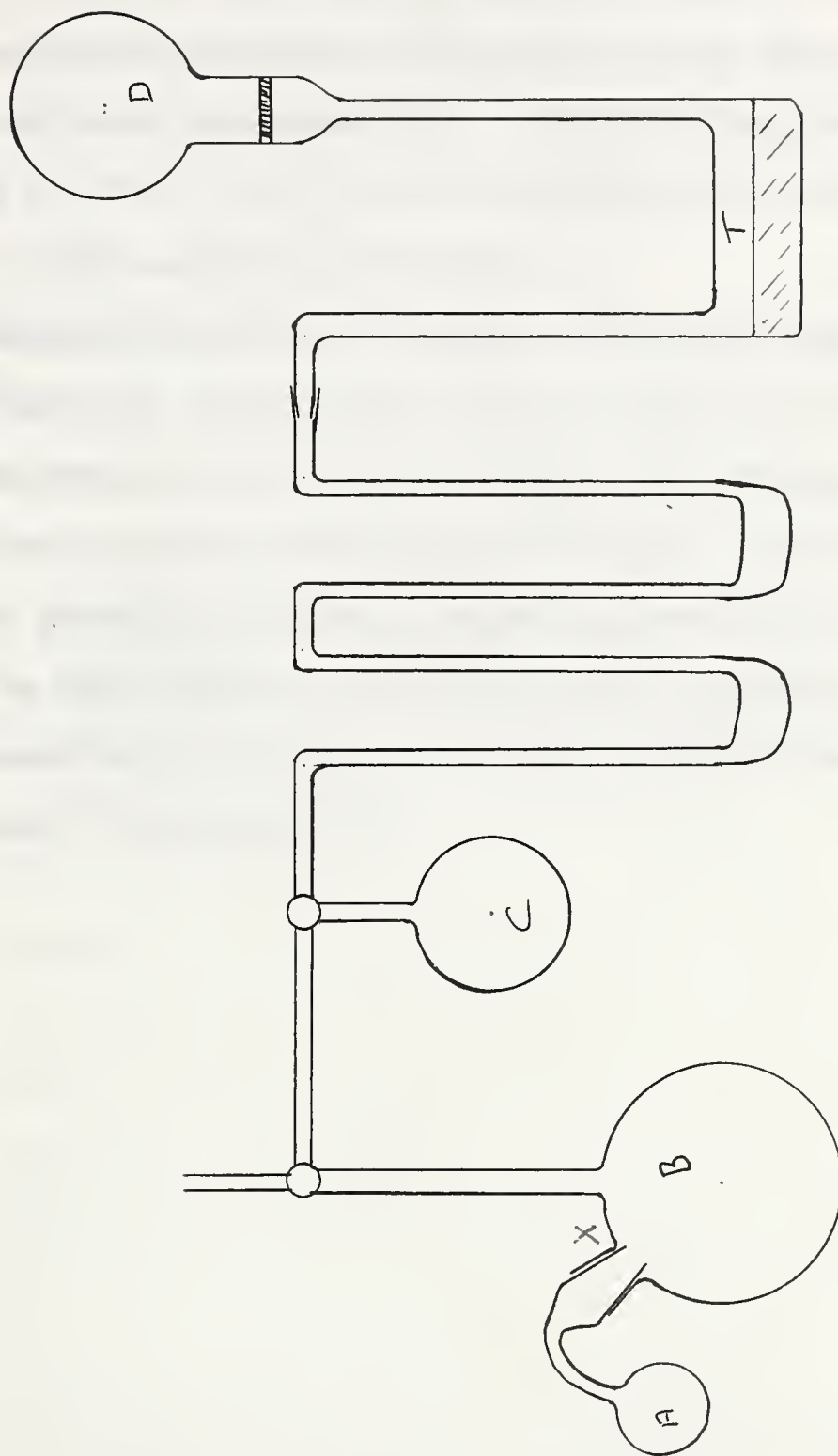


Fig. XXVII Apparatus For The Preparation of Deuteroperchloric Acid

pressure in D was below atmospheric, the admission of air into the apparatus above the silver chloride suspension forced the deuteroperchloric acid through the sintered disc into D, which was then sealed off below the sintered disc. The deuteroperchloric acid was diluted to 100 ml. with D_2O and the resultant solution was standardised against 0.05N sodium hydroxide before use.

Deuteroperchloric acid prepared in the above manner gave no precipitate with either sodium chloride or silver perchlorate solutions, although with the former reagent a very slight opalescence was observed. A solution containing approximately 10^{-6} mole.l⁻¹ of silver perchlorate in 0.4N. perchloric acid gave a deeper opalescence with sodium chloride under the same conditions, and thus it may be concluded that the deuteroperchloric acid contains no excess chloride ions, and less than 10^{-6} mole.l⁻¹ of silver ions.

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APPENDIX ITHE CALCULATION OF ΔH^\ddagger AND ΔS^\ddagger

The values shown in Table XVI are:

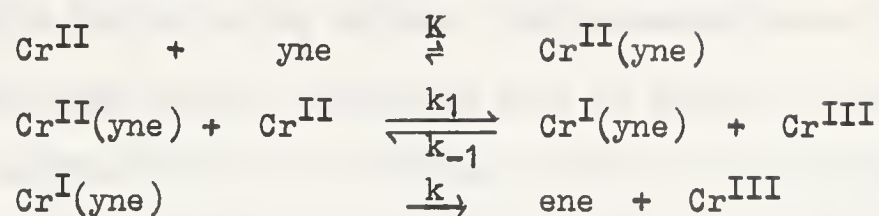
$(T^\circ K)^{-1}$	$\log k$
3.300×10^{-3}	-6.1×10^{-2}
3.247×10^{-3}	-0.3×10^{-2}
3.195×10^{-3}	6.5×10^{-2}
3.145×10^{-3}	11.7×10^{-2}
3.096×10^{-3}	18.8×10^{-2}
$\sum T^{-1} = 1.538 \times 10^{-2}$	$\sum (T^{-1})^2 = 5.112 \times 10^{-5}$
$\sum \log k = 3.06 \times 10^{-1}$	$\sum (\log k)^2 = 5.70 \times 10^{-2}$
$\sum (T^{-1}) \log k = 9.466 \times 10^{-4}$	
$\sum (T^{-1})^2 = 2.602 \times 10^{-8}$	$\sum (\log k)^2 = 3.83 \times 10^{-2}$
$\sum (T^{-1}) \log k = 3.151 \times 10^{-5}$	
$r^2 = 0.998$	$\therefore S^2(\widehat{\log k}) = 3.061 \times 10^{-5}$
$\therefore S^2(m) = 11.8 \times 10^2$	$\therefore S(m) = 0.011 \times 10^3$
$\therefore m = -(1.21 \pm 0.03) \times 10^3$	
$\therefore E_a = (5.54 \pm 0.12) \times 10^3 \text{ cal/mole}$	
$S^2(\overline{\log k}) = 6.12 \times 10^{-6}$	$\therefore S(\overline{\log k}) = 2.47 \times 10^{-3}$
$\therefore \overline{\log k} = (6.12 \pm 0.74) \times 10^{-2}$	
$\therefore c = 3.94 \pm 0.1$	

From the values of E_a and \underline{c} given above, the following values for ΔH^\ddagger and ΔS^\ddagger may be calculated.

$$\Delta H^\ddagger = 4.94 \pm 0.12 \text{ kcal/mole}$$

$$\Delta S^\ddagger = -42.6 \pm 0.4 \text{ eu/mole}$$

APPENDIX II

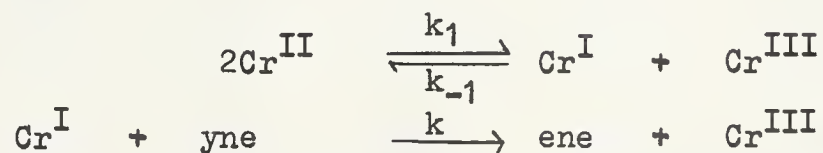
STEADY STATE CALCULATIONSPathways III and IV

$$[\text{Cr}^{\text{II}}(\text{yne})] = K[\text{Cr}^{\text{II}}][\text{yne}]$$

$$\frac{d[\text{Cr}^{\text{I}}(\text{yne})]}{dt} = k_1 K [\text{Cr}^{\text{II}}][\text{yne}] - k_{-1} [\text{Cr}^{\text{I}}(\text{yne})][\text{Cr}^{\text{III}}] - k [\text{Cr}^{\text{I}}(\text{yne})]$$

$$[\text{Cr}^{\text{I}}(\text{yne})] = \frac{K k_1 [\text{Cr}^{\text{II}}]^2 [\text{yne}]}{k_{-1} [\text{Cr}^{\text{III}}] + k}$$

$$\text{Rate} = \frac{K k_1 k [\text{Cr}^{\text{II}}]^2 [\text{yne}]}{k_{-1} [\text{Cr}^{\text{III}}] + k}$$

Pathway VII

$$\frac{d[\text{Cr}^{\text{I}}]}{dt} = k_1 [\text{Cr}^{\text{II}}]^2 - k_{-1} [\text{Cr}^{\text{I}}][\text{Cr}^{\text{III}}] - k [\text{Cr}^{\text{I}}][\text{yne}]$$

$$[\text{Cr}^{\text{I}}] = \frac{k_1 [\text{Cr}^{\text{II}}]^2}{k_{-1} [\text{Cr}^{\text{III}}] + k [\text{yne}]}$$

$$\text{Rate} = \frac{k k_1 [\text{Cr}^{\text{II}}]^2 [\text{yne}]}{k_{-1} [\text{Cr}^{\text{III}}] + k [\text{yne}]}$$

APPENDIX III

TABULATED RESULTS OF KINETIC RUNS

The kinetic runs which have been used in this thesis will be found in the following tables. The concentration of potassium dichromate used for the titrations will be found at the head of each table, together with the conditions in the solution at the start of the run. $(a-x)$ is equal to one half of the chromium (II) ion concentration and $(b-x)$ is the concentration of the organic substrate in moles per litre. Time is given in seconds.

RUN A₂

$$(\text{Cr}^{\text{II}})_0 = 8.44 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Ionic Strength} = 0.50$$

$$(\text{yne})_0 = 1.11 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Temperature} = 40.0^\circ$$

$$(\text{K}_2\text{Cr}_2\text{O}_7) = 0.5668 \text{ g.l}^{-1}$$

$$(\text{AcOH}) = 1.6 \text{ mole.l}^{-1}$$

$$\text{pH} = 1.40$$

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	$4k_3$
0	35.15	4.22	1.11	0	0	
250	34.9	4.19	1.08	0.03	1,500	6.00
750	34.6	4.15	1.04	0.07	3,660	5.12
1250	34.3	4.12	1.01	0.10	5,430	4.70
1750	33.9	4.07	0.96	0.15	8,450	4.84
2500	33.4	4.01	0.90	0.21	12,400	4.96
3200	33.1	3.97	0.86	0.25	15,200	4.75
4000	32.7	3.92	0.81	0.30	19,100	4.78
5000	32.2	3.86	0.75	0.36	24,200	4.84
6000	31.8	3.82	0.71	0.40	27,900	4.65
7000	31.3	3.76	0.65	0.46	34,000	4.86

$$k_3 = 1.23 \pm 0.08 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$$

RUN A₄

$$(\text{Cr}^{\text{II}})_0 = 8.44 \times 10^{-3} \text{ mole.l}^{-1}$$

Ionic Strength = 0.50

$$(\text{yne})_0 = 1.11 \times 10^{-3} \text{ mole.l}^{-1}$$

Temperature = 40.0°

$$(\text{K}_2\text{Cr}_2\text{O}_7)_0 = 0.5668 \text{ g.l}^{-1}$$

pH = 1.40

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	$4 k_3$
0	35.15	4.22	1.11	0	0	
250	34.9	4.19	1.08	0.03	1,500	6.00
700	34.6	4.15	1.04	0.07	3,660	5.23
1000	34.3	4.12	1.01	0.10	5,430	5.43
1500	33.9	4.07	0.96	0.15	8,450	5.63
2000	33.6	4.03	0.92	0.19	11,000	5.50
2500	33.4	4.01	0.90	0.21	12,400	4.96
3000	33.1	3.97	0.86	0.25	15,200	5.07
4000	32.5	3.90	0.79	0.32	20,700	5.17
5000	31.9	3.83	0.72	0.39	26,900	5.38
6000	31.4	3.77	0.66	0.45	32,900	5.49

$$k_3 = 1.33 \pm 0.1 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$$

RUN B₄

$(Cr^{II})_0 = 3.98 \times 10^{-3} \text{ mole. l}^{-1}$
 $(yne)_0 = 1.34 \times 10^{-3} \text{ mole. l}^{-1}$
 $(K_2Cr_2O_7)_0 = 0.5668 \text{ g.l}^{-1}$

$(AcOH) = 1.6 \text{ mole.l}^{-1}$
 $pH = 1.40$

$Ionic \text{ Strength} = 0.50$
 $Temperature = 40.0^{\circ}$

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	$4k_3$
0	33.16	3.98	1.34	0	0	
375	32.9	3.95	1.31	0.03	1,550	4.13
900	32.6	3.91	1.27	0.07	3,650	4.05
1500	32.2	3.86	1.22	0.12	6,210	4.14
2000	31.9	3.83	1.19	0.15	7,820	3.91
2500	31.5	3.78	1.14	0.20	10,800	4.32
3200	31.2	3.74	1.10	0.24	13,400	4.19
4000	30.8	3.70	1.06	0.28	16,000	4.00
5000	30.2	3.62	0.98	0.36	21,900	4.38
6000	29.8	3.58	0.94	0.40	25,200	4.20

$k_3 = 1.03 \pm 0.04 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$

RUN C₃

$$(\text{Cr}^{\text{II}})_0 = 8.04 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Ionic Strength} = 0.50$$

$$(\text{yne})_0 = 1.01 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Temperature} = 40.0^\circ$$

$$(\text{K}_2\text{Cr}_2\text{O}_7) = 0.5668 \text{ g.l}^{-1}$$

$$(\text{AcOH}) = 1.6 \text{ mole.l}^{-1}$$

$$\text{pH} = 1.40$$

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	$4 k_3$
0	33.5	4.02	1.01	0	0	
250	33.3	4.00	0.99	0.02	1,120	4.48
900	33.0	3.96	0.95	0.06	3,690	4.10
1500	32.7	3.92	0.91	0.10	6,480	4.32
2000	32.5	3.90	0.89	0.12	7,980	3.99
3000	32.0	3.84	0.83	0.18	12,600	4.20
4000	31.6	3.79	0.78	0.23	16,900	4.24
5000	31.3	3.76	0.75	0.26	18,900	3.77
6000	30.8	3.70	0.69	0.32	25,700	4.28

$$k_3 = 1.04 \pm 0.05 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$$

RUN E₁

$$(\text{Cr}^{\text{II}})_0 = 22.36 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Ionic Strength} = 0.50$$

$$(\text{yne})_0 = 1.35 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Temperature} = 45.0^\circ$$

$$(\text{K}_2\text{Cr}_2\text{O}_7) = 1.3606 \text{ g.l}^{-1}$$

$$(\text{AcOH}) = 3.3 \text{ mole.l}^{-1}$$

$$\text{pH} = 1.75$$

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	$4k_3$
0	38.9	11.18	1.35	0	0	
95	38.1	10.95	1.12	0.23	15,500	16.3
250	37.1	10.66	0.83	0.52	41,100	16.4
460	36.2	10.40	0.57	0.78	75,030	16.3
860	35.2	10.12	0.29	1.06	139,000	16.2

$$k_3 = 16.3 \pm 0.1 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$$

RUN H₁

$$(\text{Cr}^{\text{II}})_0 = 3.820 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Ionic Strength} = 0.50$$

$$(\text{yne})_0 = 0.700 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Temperature} = 45.0^\circ$$

$$(\text{K}_2\text{Cr}_2\text{O}_7) = 0.3007 \text{ g.l}^{-1}$$

$$(\text{AcOH}) = 1.6 \text{ mole.l}^{-1}$$

$$\text{pH} = 1.40$$

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	4k ₃
0	30.00	1.910	0.700	0	0	
600	29.90	1.903	0.693	0.007	2,770	4.62
1100	29.80	1.897	0.687	0.013	5,180	4.71
1900	29.65	1.888	0.678	0.022	8,880	4.67
2800	29.50	1.878	0.668	0.032	13,090	4.68
4300	29.25	1.862	0.652	0.048	20,000	4.65
6200	28.95	1.843	0.633	0.067	28,700	4.63
9850	28.40	1.808	0.598	0.102	45,700	4.64

$$k_3 = 1.16 \pm 0.03 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$$

RUN H₃

$(Cr^{II})_0 = 3.820 \times 10^{-3} \text{ mole.l}^{-1}$ Ionic Strength = 0.50

$(yne)_0 = 1.910 \times 10^{-3} \text{ mole.l}^{-1}$ Temperature = 45.0°

$(K_2Cr_2O_7) = 0.2905 \text{ g.l}^{-1}$ $(AcOH) = 1.6 \text{ mole.l}^{-1}$ pH = 1.40

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^3}$	4k ₃
0	31.05	1.910	3.820	0	0	
90	31.00	1.907	3.817	0.003	430	4.44
280	30.90	1.901	3.811	0.009	1,300	4.64
980	30.55	1.879	3.789	0.031	4,560	4.65
2,000	30.05	1.848	3.758	0.062	9,350	4.68
3,000	29.95	1.818	3.728	0.092	14,200	4.73
5,300	28.60	1.759	3.669	0.151	24,600	4.64
9,500	27.00	1.661	3.571	0.249	44,200	4.65
15,800	25.05	1.541	3.451	0.369	73,500	4.65
27,800	22.30	1.372	3.282	0.538	128,600	4.64

$k_3 = 1.15 \pm 0.02 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$

RUN H₅

$$(\text{Cr}^{\text{II}})_0 = 3.82 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Ionic Strength} = 0.50$$

$$(\text{yne})_0 = 5.35 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Temperature} = 45.0^{\circ}$$

$$(\text{K}_2\text{Cr}_2\text{O}_7) = 0.2905 \text{ g.l}^{-1} \quad (\text{AcOH}) = 1.6 \text{ mole.l}^{-1} \quad \text{pH} = 1.40$$

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	$4k_3$
0	31.05	1.910	5.350	0	0	
70	30.95	1.904	5.344	0.006	310	4.43
300	30.60	1.882	5.322	0.028	1,450	4.83
820	29.90	1.839	5.279	0.071	3,810	4.65
1,300	29.25	1.799	5.239	0.111	6,100	4.69
2,560	27.75	1.707	5.147	0.203	11,900	4.65
3,900	26.30	1.618	5.058	0.292	18,200	4.67
7,000	23.60	1.452	4.892	0.458	32,400	4.63
13,000	19.70	1.212	4.652	0.698	61,100	4.70
21,500	16.25	1.000	4.440	0.910	99,500	4.63
33,200	14.15	0.809	4.249	1.101	153,900	4.64
52,000	10.20	0.627	4.067	1.283	240,000	4.62
79,000	7.75	0.477	3.917	1.433	366,000	4.63

$$k_3 = 1.15 \pm 0.02 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$$

RUN R₃

$$(\text{Cr}^{\text{II}})_0 = 2.778 \times 10^{-2} \text{ mole.l}^{-1}$$

Ionic Strength = 0.50

$$(\text{yne})_0 = 1.099 \times 10^{-2} \text{ mole.l}^{-1}$$

Temperature = 40.0°

$$(\text{K}_2\text{Cr}_2\text{O}_7) = 1.2820 \text{ g.l}^{-1} \quad (\text{Cr}^{\text{III}})_0 = 3 \times 10^{-2} \text{ mole.l}^{-1} \cdot \text{pH} = 4.30$$

time (secs)	Titre (ml.)	$10^{-2} \cdot (a-x)$ mole.l ⁻¹	$10^{-2} \cdot (b-x)$ mole.l ⁻¹	$10^{-2} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	4k ₃
0	41.60	1.389	1.099	0	0	
90	41.60	-----	-----	-----	-----	-----
300	41.35	1.381	1.091	0.008	31	0.104
900	40.75	1.361	1.071	0.028	131	0.156
1500	40.25	1.344	1.054	0.045	223	0.149
2400	39.55	1.321	1.031	0.068	351	0.146
5400	37.40	1.249	0.959	0.140	790	0.146

$$k_3 = 0.0373 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$$

RUN K₇

$$(\text{Cr}^{\text{II}})_0 = 7.978 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Ionic Strength} = 0.50$$

$$(\text{yne})_0 = 1.750 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Temperature} = 40.0^\circ$$

$$(\text{K}_2\text{Cr}_2\text{O}_7) = 4.7190 \text{ g.l}^{-1}$$

$$(\text{AcOH}) = 0.30 \text{ mole.l}^{-1}$$

$$\text{pH} = 1.40$$

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	4k ₃
0	3.992	3.989	1.750	0	0	
200	3.980	3.977	1.738	0.012	440	2.19
600	3.935	3.932	1.693	0.057	2,190	3.66
1000	3.900	3.897	1.658	0.092	3,450	3.45
1400	3.845	3.842	1.603	0.147	5,430	4.09
1800	3.775	3.772	1.533	0.217	8,800	4.89
2200	3.755	3.752	1.513	0.237	9,730	4.42
2600	3.695	3.692	1.453	0.297	12,660	4.87
3000	3.685	3.682	1.443	0.307	13,200	4.39
3400	3.670	3.667	1.428	0.322	13,900	4.10
3800	3.605	3.602	1.363	0.387	17,500	4.60
4200	3.580	3.577	1.338	0.412	18,900	4.50
4600	3.560	3.557	1.318	0.429	20,100	4.37
5000	3.515	3.512	1.273	0.477	22,900	4.58
5800	3.460	3.457	1.218	0.532	26,500	4.57
6200	3.430	3.427	1.188	0.562	28,600	4.61

$$k_3 = 1.18 \pm 0.02 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$$

RUN K₈

$$(\text{Cr}^{\text{II}})_0 = 1.042 \times 10^{-2} \text{ mole.l}^{-1}$$

$$\text{Ionic Strength} = 0.50$$

$$(\text{yne})_0 = 2.947 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Temperature} = 40.0^\circ$$

$$(\text{K}_2\text{Cr}_2\text{O}_7) = 0.7888 \text{ g.l}^{-1}$$

$$(\text{AcOH}) = 0.70 \text{ mole.l}^{-1}$$

$$\text{pH} = 1.40$$

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	$4k_3$
0	31.20	5.210	2.947	0	0	
70	31.05	5.185	2.922	0.025	310	4.44
480	30.25	5.052	2.789	0.158	2,080	4.33
960	29.40	4.910	2.647	0.300	4,180	4.35
1440	28.60	4.776	2.513	0.434	6,360	4.32
1920	27.85	4.651	2.388	0.559	8,700	4.53
2400	27.25	4.551	2.288	0.659	10,700	4.46
3000	26.45	4.417	2.514	0.793	13,800	4.60
3600	26.00	4.342	2.079	0.868	15,500	4.31
4620	24.95	4.167	1.904	1.043	20,500	4.44
6420	23.55	3.933	1.670	1.277	28,500	4.44

$$k_3 = 1.11 \pm 0.02 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$$

RUN S₁₀

$(Cr^{II})_0 = 2.756 \times 10^{-2} \text{ mole.l}^{-1}$

Ionic Strength = 1.20

$(yne)_0 = 1.378 \times 10^{-2} \text{ mole.l}^{-1}$

Temperature = 45.0°

$(K_2Cr_2O_7) = 1.2820 \text{ g.l}^{-1}$

$(AcOH) = 1.6 \text{ mole.l}^{-1}$

pH = 1.40

time (secs)	Titre (ml.)	$10^{-2} \cdot (a-x)$ mole.l ⁻¹	$10^{-2} (2a-x)$ mole.l ⁻¹	$10^{-2} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^3}$	4k ₃
0	41.27	1.378	2.756	0	0	
85	38.25	1.277	2.665	0.101	433	5.09
540	28.95	0.967	2.345	0.411	2,710	5.03
1140	23.05	0.770	2.148	0.608	5,800	5.09
2160	18.20	0.608	1.968	0.770	10,890	5.04
1500	20.90	0.698	2.076	0.680	7,630	5.09
2880	16.25	0.543	1.921	0.835	14,250	4.95
3720	14.55	0.486	1.864	0.892	18,540	4.98

$$k_3 = 1.25 \pm 0.02 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$$

RUN S₁₁

$$(\text{Cr}^{\text{II}})_0 = 2.756 \times 10^{-2} \text{ mole.l}^{-1}$$

$$\text{Ionic Strength} = 0.80$$

$$(\text{yne})_0 = 1.378 \times 10^{-2} \text{ mole.l}^{-1}$$

$$\text{Temperature} = 45.0^\circ$$

$$(\text{K}_2\text{Cr}_2\text{O}_7) = 1.2820 \text{ g.l}^{-1}$$

$$(\text{AcOH}) = 1.6 \text{ mole.l}^{-1}$$

$$\text{pH} = 1.40$$

time (secs)	Titre (ml.)	$10^{-2} \cdot (a-x)$ mole.l ⁻¹	$10^{-2}(2a-x)$ mole.l ⁻¹	$10^{-2} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^3}$	$4k_3$
0	41.27	1.378	2.756	0	0	
95	38.15	1.274	2.652	0.104	447	4.71
540	29.05	0.970	2.348	0.408	2,680	4.96
1200	23.15	0.773	2.151	0.605	5,730	4.78
1560	21.05	0.703	2.081	0.675	7,480	4.80
1960	19.60	0.654	2.032	0.724	9,060	4.87
2400	18.00	0.601	1.979	0.777	11,200	4.67
3000	16.00	0.534	1.912	0.844	14,850	4.95
3660	14.85	0.496	1.874	0.882	17,700	4.84

$$k_3 = 1.20 \pm 0.02 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$$

RUN S₁₂

$(\text{Cr}^{\text{II}})_0 = 2.756 \times 10^{-2} \text{ mole.l}^{-1}$
 $(\text{yne})_0 = 1.378 \times 10^{-2} \text{ mole.l}^{-1}$
 $(\text{K}_2\text{Cr}_2\text{O}_7) = 1.2820 \text{ g.l}^{-1}$

$\text{Ionic Strength} = 0.30$
 $\text{Temperature} = 45.0^\circ$
 $(\text{AcOH}) = 1.6 \text{ mole.l}^{-1}$
 $\text{pH} = 1.40$

time (secs)	Titre (ml.)	$10^{-2} \cdot (a-x)$ mole.l ⁻¹	$10^{-2} (2a-x)$ mole.l ⁻¹	$10^{-2} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^3}$	$4k_3$
0	41.27	1.378	2.756	0	0	
95	38.25	1.277	2.605	0.101	425	4.47
580	29.10	0.972	2.350	0.406	2,660	4.59
1200	23.35	0.780	2.158	0.598	5,580	4.65
1540	21.50	0.718	2.096	0.660	7,060	4.58
1860	20.05	0.669	2.047	0.709	8,530	4.59
2250	18.65	0.623	2.001	0.755	10,250	4.56
3000	16.55	0.553	1,931	0.825	13,720	4.57
3600	15.45	0.516	1.894	0.862	16,150	4.49

$k_3 = 1.14 \pm 0.02 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$

RUN N₂₃

$(Cr^{II})_0 = 5.540 \times 10^{-3} \text{ mole.l}^{-1}$
 $(yne)_0 = 1.835 \times 10^{-3} \text{ mole.l}^{-1}$
 $(K_2Cr_2O_7) = 0.6211 \text{ g.l}^{-1}$
 $(Cr^{III})_0 = 2.8 \times 10^{-2} \text{ mole.l}^{-1}$

Ionic Strength = 0.50

Temperature = 40.0°

pH = 1.40

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	4k ₃
0	21.06	2.770	1.835	0	0	
300	20.95	2.755	1.820	0.015	1,110	3.72
600	20.80	2.735	1.800	0.035	2,600	4.33
900	20.65	2.715	1.780	0.055	4,100	4.55
1200	20.60	2.709	1.774	0.061	4,620	3.85
1500	20.45	2.689	1.754	0.081	6,220	4.15
1800	20.35	2.676	1.741	0.094	7,210	4.01
2400	20.10	2.643	1.708	0.127	9,890	4.12
3000	19.85	2.610	1.765	0.160	12,720	4.24
3600	19.65	2.584	1.649	0.186	15,000	4.16
5400	19.05	2.505	1.570	0.265	22,600	4.18
7500	18.50	2.433	1.498	0.337	30,400	4.05
11,400	17.45	2.295	1.360	0.475	47,700	4.19

$k_3 = 1.04 \pm 0.02 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$

RUN N₂₄

$(Cr^{II})_0 = 5.504 \times 10^{-3} \text{ mole.l}^{-1}$
 $(yne)_0 = 1.687 \times 10^{-3} \text{ mole.l}^{-1}$
 $(K_2Cr_2O_7) = 0.6211 \text{ g.l}^{-1}$
 $(Cr^{III})_0 = 8.7 \times 10^{-2} \text{ mole.l}^{-1}$

Ionic Strength = 0.50

Temperature = 40.0°

$(AcOH) = 1.6 \text{ mole.l}^{-1}$
pH = 1.40

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\left(\frac{dx}{(a-x)^2(b-x)} \right)$	4k ₃
0	20.93	2.752	1.687	0	0	
600	20.70	2.722	1.657	0.030	2,400	4.00
1200	20.45	2.689	1.624	0.063	5,160	4.30
1800	20.20	2.656	1.591	0.096	8,010	4.45
2400	20.05	2.637	1.572	0.115	9,740	4.06
3000	19.85	2.610	1.545	0.142	12,200	4.07
3600	19.65	2.584	1.519	0.168	14,800	4.11
5400	19.15	2.518	1.453	0.234	21,600	4.00
7200	18.60	2.446	1.381	0.306	29,900	4.15
9000	18.15	2.387	1.322	0.365	34,300	4.15
15,000	16.80	2.209	1.144	0.543	64,800	4.32

k₃ = 1.04 ± 0.02 l².mole⁻².sec⁻¹

RUN S₂

$$(\text{Cr}^{\text{II}})_0 = 1.054 \times 10^{-2} \text{ mole.l}^{-1}$$

$$\text{Ionic Strength} = 0.50$$

$$(\text{yne})_0 = 4.949 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Temperature} = 40.0^\circ$$

$$(\text{K}_2\text{Cr}_2\text{O}_7) = 1.2820 \text{ g.l}^{-1}$$

$$\text{pH} = 1.40$$

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\left(\frac{dx}{(a-x)^2(b-x)} \right)$	$4k_3$
0	15.78	5.269	4.949	0	0	
60	15.68	5.236	4.916	0.033	80	1.33
360	15.27	5.099	4.779	0.170	1,600	4.44
660	14.63	4.885	3.565	0.384	3,080	4.67
1500	13.71	4.578	4.258	0.691	6,760	4.57
2400	12.78	4.267	3.947	1.002	10,970	4.57
3600	11.85	3.957	3.637	1.312	13,100	3.64
6900	9.75	3.256	2.936	2.013	32,300	4.68
9000	8.93	2.982	2.662	2.287	42,200	4.69
12,600	8.01	2.675	2.355	2.594	58,200	4.62

$$k_3 = 1.33 \pm 0.03 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$$

RUN S₃

$(Cr^{II})_0 = 1.046 \times 10^{-2} \text{ mole.l}^{-1}$
 $(yne)_0 = 2.969 \times 10^{-3} \text{ mole.l}^{-1}$
 $(K_2Cr_2O_7) = 0.6410 \text{ g.l}^{-1}$

Ionic Strength = 0.50

Temperature = 40.0°

pH = 1.40

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	4k ₃
0	31.35	5.235	2.969	0	0	
90	31.10	5.194	2.928	0.041	500	5.56
390	30.40	5.077	2.811	0.158	2,040	5.23
870	29.35	4.901	2.635	0.334	4,650	5.35
1620	28.05	4.684	2.418	0.551	8,400	5.20
2160	27.10	4.526	2.260	0.709	11,600	5.37
3600	25.35	4.233	1.967	1.002	18,800	5.22
5400	23.50	3.925	1.659	1.310	29,100	5.39
7920	21.70	3.624	1.358	1.611	43,200	5.45
8500	21.55	3,599	1.323	1.646	45,800	5.39

k₃ = 1.34 ± 0.03 l².mole⁻².sec⁻¹

RUN T₃

$(Cr^{II})_0 = 8.652 \times 10^{-3} \text{ mole.l}^{-1}$
 $(yne)_0 = 2.912 \times 10^{-3} \text{ mole.l}^{-1}$
 $(K_2Cr_2O_7) = 0.3322 \text{ g.l}^{-1}$

$pH = 0.20$

$Ionic \text{ Strength} = 0.50$
 $Temperature = 40.0^{\circ}$
 $(H_3O^+) = 0.631$

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	$4k_3$
0	61.51	4.326	2.912	0	0	
280	61.20	4.305	2.891	0.021	350	1.25
780	60.75	4.273	2.859	0.053	970	1.24
1,300	60.25	4.238	2.824	0.088	1,620	1.25
2,000	59.55	4.189	2.775	0.137	2,590	1.30
2,900	58.95	4.147	2.733	0.179	3,540	1.22
3,600	58.35	4.104	2.690	0.222	4,430	1.23
5,000	57.20	4.023	2.609	0.303	6,310	1.26
7,500	55.65	3.914	2.500	0.412	9,000	1.20
10,000	54.00	3.798	2.384	0.528	12,200	1.22
13,000	52.40	3.686	2.272	0.640	16,300	1.25
18,000	49.75	3.499	2.085	0.827	22,300	1.24
25,000	46.95	3.302	1.888	1.024	30,900	1.24

$k_3 = 0.310 \pm 0.005 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$

RUN T₄

$(Cr^{II})_0 = 6.446 \times 10^{-3} \text{ mole.l}^{-1}$
 $(yne)_0 = 2.912 \times 10^{-3} \text{ mole.l}^{-1}$
 $(K_2Cr_2O_7) = 0.3322 \text{ g.l}^{-1}$

$(H_3O^+) = 0.178 \text{ mole.l}^{-1}$
 $pH = 0.75$

$Ionic\ Strength = 0.50$
 $Temperature = 40.0^{\circ}$

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	$4k_3$
0	45.82	3.223	2.912	0	0	
140	45.40	3.193	2.882	0.030	860	6.14
900	43.80	3.081	2.770	0.142	5,660	6.29
1400	52.50	2.989	2.678	0.234	8,290	5.92
2000	41.00	2.884	2.537	0.339	13,200	6.60
3100	39.55	2.782	2.471	0.441	19,200	6.19
4000	38.00	2.673	2.362	0.550	24,600	6.15
5500	36.05	2.536	2.225	0.687	33,800	6.15
7000	34.15	2.402	2.091	0.821	43,700	6.24
9000	31.85	2.240	1.929	0.983	57,800	6.42
12,000	29.50	2.075	1.764	1.148	77,600	6.47

$k_3 = 1.56 \pm 0.03 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$

RUN T₅

$$(\text{Cr}^{\text{II}})_0 = 4.248 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Ionic Strength} = 0.50$$

$$(\text{yne})_0 = 2.910 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Temperature} = 40.0^\circ$$

$$(\text{K}_2\text{Cr}_2\text{O}_7) = 0.3322 \text{ g.l}^{-1}$$

$$\text{pH} = 1.40$$

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	$4k_3$
0	30.19	2.124	2.910	0	0	
400	27.70	1.948	2.734	0.176	16,200	40.5
900	25.20	1.773	2.559	0.351	35,600	39.6
1500	22.70	1.597	2.383	0.527	60,600	40.4
2400	20.25	1.424	2.210	0.700	94,000	39.2
3400	18.10	1.273	2.059	0.851	133,000	39.2
4600	16.05	1.129	1.915	0.995	184,000	39.9
6000	14.35	1.009	1.795	1.115	241,000	40.1
7700	12.85	0.904	1.690	1.220	307,000	39.9

$$k_3 = 9.95 \pm 0.09 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$$

RUN T₆

$(Cr^{II})_0 = 4.238 \times 10^{-3} \text{ mole.l}^{-1}$

Ionic Strength = 0.50

$(yne)_0 = 1.456 \times 10^{-3} \text{ mole.l}^{-1}$

Temperature = 40.0°

$(K_2Cr_2O_7) = 0.3322 \text{ g.l}^{-1}$

pH = 1.85

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	4k ₃
0	30.11	2.019	1.456	0	0	
330	26.35	1.853	1.190	0.266	52,600	159
850	22.65	1.593	0.930	0.526	136,000	160
1200	20.95	1.474	0.811	0.645	194,000	162
1700	19.20	1.351	0.688	0.768	277,000	163
2400	1.780	1.252	0.589	0.867	369,000	154
2900	16.75	1,178	0.515	0.941	460,000	159

$k_3 = 39.8 \pm 0.4 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$

RUN T₇

$$(\text{Cr}^{\text{II}})_0 = 2.038 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Ionic Strength} = 0.50$$

$$(\text{yne})_0 = 1.453 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Temperature} = 40.0^\circ$$

$$(\text{K}_2\text{Cr}_2\text{O}_7) = 0.3322 \text{ g.l}^{-1}$$

$$\text{pH} = 2.15$$

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	$4k_3$
0	28.97	1019	1.453	0	0	
60	28.80	0.985	1.419	0.034	23,600	393
360	24.00	0.844	1.278	0.175	136,000	378
800	20.05	0.705	1.139	0.314	330,000	413
1200	18.20	0.640	1.074	0.379	475,000	396
1600	16.50	0.580	1.014	0.439	633,000	396
2000	14.85	0.522	0.956	0.497	826,000	413
3000	12.65	0.445	0.879	0.574	1,189,000	396

$$k_3 = 99.5 \pm 0.9 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$$

RUN T₈

$(Cr^{II})_0 = 8.630 \times 10^{-3} \text{ mole.l}^{-1}$

Ionic Strength = 0.50

$(yne)_0 = 3.644 \times 10^{-3} \text{ mole.l}^{-1}$

Temperature = 40.0°

$(K_2Cr_2O_7) = 0.3322 \text{ g.l}^{-1}$

pH = 1.45

Time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	4k ₃
0	61.35	4.315	3.644	0	0	
200	61.15	4.301	3.630	0.014	200	1.00
600	60.74	4.273	3.602	0.042	590	0.98 ₃
1,000	60.35	4.245	3.473	0.070	950	0.95 ₁
1,400	59.95	4.217	3.546	0.098	1,480	1.06
2,000	59.45	4.182	3.511	0.133	2,120	1.06
6,000	56.20	3.943	3.282	0.362	6,020	1.00
10,000	53.30	3.749	3.078	0.566	10,460	1.05
15,000	50.55	3.556	2.885	0.759	15,400	1.02
21,000	47.95	3.373	2.702	0.942	20,800	0.99 ₀
30,000	44.80	3.151	2.480	1.164	28,900	0.96 ₃

k₃ = 0.243 ± 0.003 l².mole⁻².sec⁻¹

RUN T₉

$$(\text{Cr}^{\text{II}})_0 = 8,602 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Ionic Strength} = 0.50$$

$$(\text{yne})_0 = 2.915 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Temperature} = 40.0^\circ$$

$$(\text{K}_2\text{Cr}_2\text{O}_7) = 0.3322 \text{ g.l}^{-1}$$

$$\text{pH} = 1.80$$

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	$4k_3$
0	61.14	4.301	2.915	0	0	
250	60.55	4.259	2.873	0.042	740	2.96
650	59.65	4.196	2.810	0.105	1,970	3.03
1200	58.70	4.129	2.743	0.172	3,380	2.82
1600	57.65	4.055	2.669	0.246	5,020	3.13
2100	56.85	3.999	2.613	0.302	6,360	3.03
3000	55.20	3.883	2.497	0.418	9,310	3.10
4000	53.65	3.774	2.388	0.527	12,300	3.07
5000	52.15	3.668	2.282	0.633	15,600	3.13
6000	51.00	3.587	2.201	0.714	18,300	3.05
7000	50.00	3.571	2.131	0.784	20,900	2.99
8000	49.00	3.447	2.061	0.854	23,700	2.97
9000	48.00	3.376	1.990	0.925	26,700	2.97
10,000	47.00	3.306	1.920	0.995	30,000	3.00

$$k_3 = 0.75_5 \pm 0.007 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$$

RUN T₁₀

$$(\text{Cr}^{\text{II}})_0 = 8.602 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Ionic Strength} = 0.50$$

$$(\text{yne})_0 = 2.915 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Temperature} = 40.0^\circ$$

$$(\text{K}_2\text{Cr}_2\text{O}_7) = 0.3322 \text{ g.l}^{-1}$$

$$\text{pH} = 2.20$$

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	$4k_3$
0	61.14	4.301	2.915	0	0	
160	59.65	4.196	2.810	0.105	1,970	12.3
500	56.95	4.006	2.620	0.295	6,170	12.3
1000	53.65	3.774	2.388	0.527	12,300	12.3
1500	51.10	3.594	2.208	0.707	18,100	12.1
2000	49.00	3.447	2.061	0.854	23,700	11.9
2500	47.00	3.306	1.920	0.995	30,000	12.0
3000	45.15	3.176	1.790	1.125	36,600	12.2
4500	41.65	2.930	1.544	1.371	52,600	11.7
5500	39.15	2.754	1.368	1.547	67,700	12.3

$$k_3 = 3.30 \pm 0.05 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$$

RUN T₁₁

$$(\text{Cr}^{\text{II}})_0 = 4.112 \times 10^{-3} \text{ mole.l}^{-1}$$

Ionic Strength = 0.50

$$(\text{yne})_0 = 3.644 \times 10^{-3} \text{ mole.l}^{-1}$$

Temperature = 40.0°

$$(\text{K}_2\text{Cr}_2\text{O}_7) = 0.3322 \text{ g.l}^{-1}$$

pH = 2.60

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\frac{dx}{(a-x)^2(b-x)}$	4k ₃
0	29.94	2.106	3.644	0	0	
110	29.90	2.040	3.578	0.066	4,280	38.9
750	24.85	1.748	3.286	0.358	28,200	37.6
1400	21.75	1.530	3.068	0.576	53,900	38.5
2300	18.80	1.322	2.860	0.784	88,700	38.6
3500	16.15	1.136	2.674	0.970	134,000	38.3
4800	14.30	1.005	2.545	1.099	177,000	36.9
6000	12.45	0.876	2.414	1.230	236,000	39.4

$$k_3 = 9.50 \pm 0.2 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$$

RUN T₁₂

$$(\text{Cr}^{\text{II}})_0 = 1.954 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Ionic Strength} = 0.50$$

$$(\text{yne})_0 = 2.186 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Temperature} = 40.0^\circ$$

$$(\text{K}_2\text{Cr}_2\text{O}_7) = 0.1661 \text{ g.l}^{-1}$$

$$\text{pH} = 3.20$$

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	$4k_3$
0	27.79	0.977	2.186	0	0	
120	26.65	0.937	2.146	0.040	20,400	170
700	22.80	0.802	2.011	0.175	107,000	153
1600	18.95	0.666	1.875	0.311	238,000	149
2100	17.10	0.601	1.810	0.376	327,000	156
3000	15.05	0.529	1.738	0.448	454,000	151
4000	13.15	0.462	1.671	0.515	616,000	154
5300	11.45	0.403	1.612	0.574	808,000	152

$$k_3 = 38.0 \pm 0.5 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$$

RUN T₁₃

$(Cr^{II})_0 = 1.942 \times 10^{-3}$
 $(yne)_0 = 0.729 \times 10^{-3}$
 $(K_2Cr_2O_7) = 0.1661 \text{ g.l}^{-1}$

Ionic Strength = 0.50

Temperature = 40.0°

pH = 4.20

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	4k ₃
0	27.60	0.971	0.729	0	0	
110	22.35	0.786	0.544	0.185	3,900	3540
300	18.05	0.635	0.393	0.336	10,600	3530
550	15.10	0.531	0.289	0.440	19,700	3580
750	13.65	0.480	0.238	0.491	27,300	3640
1000	12.55	0.441	0.199	0.530	35,700	3570

$k_3 = 890 \pm 20 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$

RUN Q₁

$(Cr^{II})_0 = 2.142 \times 10^{-2} \text{ mole.l}^{-1}$
 $(yne)_0 = 0.459 \times 10^{-2} \text{ mole.l}^{-1}$
 $(K_2Cr_2O_7) = 1.2820 \text{ g.l}^{-1}$

$(H_3O^+) = 0.500 \text{ mole.l}^{-1}$
 $pH = 0.30$

$Ionic \text{ Strength} = 0.51$
 $Temperature = 40.0^{\circ}$

time (secs)	Titre (ml.)	$10^{-2} \cdot (a-x)$ mole.l ⁻¹	$10^{-2} \cdot (b-x)$ mole.l ⁻¹	$10^{-2} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	4k ₃
0	32.08	1.071	0.459	0	0	
100	32.00	-----	-----	-	-	
400	31.95	1.067	0.455	0.004	76	0.190
800	31.75	1.060	0.448	0.011	215	0.269
2,000	31.30	1.045	0.433	0.026	523	0.262
4,200	30.55	1.020	0.408	0.051	1080	0.257
6,400	29.85	0.997	0.385	0.074	1650	0.258
9,700	28.95	0.967	0.365	0.104	2500	0.258
12,000	28.35	0.947	0.335	0.124	3130	0.261
18,000	27.15	0.907	0.295	0.164	4610	0.256
31,000	25.10	0.838	0.226	0.233	8110	0.261

$k_3 = 0.0650 \pm 0.0002 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$

RUN Q₂

$(Cr^{II})_0 = 2.142 \times 10^{-2} \text{ mole.l}^{-1}$
 $(yne)_0 = 0.459 \times 10^{-2} \text{ mole.l}^{-1}$
 $(K_2Cr_2O_7) = 1.2820 \text{ g.l}^{-1}$

$(H_3O^+) = 0.302 \text{ mole.l}^{-1}$
 $pH = 0.52$

Ionic Strength = 0.50

Temperature = 40.0°

time (secs)	Titre (ml.)	$10^{-2} \cdot (a-x)$ mole.l ⁻¹	$10^{-2} \cdot (b-x)$ mole.l ⁻¹	$10^{-2} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	$4k_3$
0	32.08	1.071	0.459	0	0	
90	31.85	1.063	0.451	0.008	156	1.73
400	31.75	1.060	0.448	0.011	215	0.537
1000	31.35	1.047	0.435	0.024	481	0.481
2100	30.55	1.020	0.408	0.051	1080	0.514
3200	29.90	0.998	0.386	0.073	1620	0.506
6000	28.45	0.950	0.338	0.121	3020	0.504
10,000	27.00	0.902	0.290	0.169	4820	0.482
16,000	25.15	0.840	0.228	0.231	7980	0.499

$k_3 = 0.126 \pm 0.003 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$

RUN Q₃

$(Cr^{II})_0 = 2.142 \times 10^{-2} \text{ mole.l}^{-1}$
 $(yne)_0 = 0.459 \times 10^{-2} \text{ mole.l}^{-1}$
 $(K_2Cr_2O_7) = 1.2820 \text{ g.l}^{-1}$

$(H_3O^+) = 0.100 \text{ mole.l}^{-1}$
 $pH = 1.00$

$Ionic\ Strength = 0.50$
 $Temperature = 40.0^{\circ}$

time (secs)	Titre (ml.)	$10^{-2} \cdot (a-x)$ mole.l ⁻¹	$10^{-2} \cdot (b-x)$ mole.l ⁻¹	$10^{-2} \cdot x$ mole.l ⁻¹	$\frac{dx}{(a-x)^2(b-x)}$	4k ₃
0	32.08	1.071	0.459	0	0	
60	31.90	1.065	0.453	0.006	116	1.94
500	30.60	1.022	0.410	0.049	1040	2.07
1050	29.35	0.980	0.368	0.091	2110	2.01
1650	28.20	0.942	0.330	0.129	3300	2.00
3200	26.05	0.870	0.258	0.201	6310	1.97
5000	24.35	0.813	0.201	0.258	9830	1.97
7000	23.00	0.768	0.156	0.303	13,900	1.99

$k_3 = 0.498 \pm 0.003 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$

RUN N₂₁

$(Cr^{II})_0 = 6.124 \times 10^{-3} \text{ mole.l}^{-1}$
 $(yne)_0 = 1.714 \times 10^{-3} \text{ mole.l}^{-1}$
 $(K_2Cr_2O_7) = 0.4731 \text{ g.l}^{-1}$

Ionic Strength = 0.50

Temperature = 40.0°

pH = 1.50

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	4k ₃
0	30.59	3.062	1.714	0	0	
46	30.50	3.053	-----	-	-	
600	29.90	2.993	1.645	0.069	4,000	7.58
1200	29.25	2.928	1.580	0.134	9,110	7.59
1800	28.65	2.868	1.520	0.194	13,690	7.60
2400	28.10	2.813	1.465	0.249	18,280	7.62
3000	27.65	2.768	1.420	0.294	22,300	7.43
3600	27.10	2.713	1.365	0.349	27,500	7.65

$k_3 = 1.90 \pm 0.02 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$

RUN N₂₂

$(\text{Cr}^{\text{II}})_0 = 5.714 \times 10^{-3} \text{ mole.l}^{-1}$
 $(\text{yne})_0 = 1.714 \times 10^{-3} \text{ mole.l}^{-1}$
 $(\text{K}_2\text{Cr}_2\text{O}_7) = 0.6328 \text{ g.l}^{-1}$

Ionic Strength = 0.50

Temperature = 40.0°

pH = 1.60

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\left\{ \frac{dx}{(a-x)^2(b-x)} \right\}$	$4k_3$
0	21.73	2.857	1.714	0	0	
180	21.75	-----	-----	-	-	
600	21.25	2.794	1.651	0.063	4,640	7.73
1200	20.75	2.729	1.586	0.128	9,850	8.21
3300	19.35	2.545	1.402	0.312	28,300	8.58
3840	19.00	2.499	1.356	0.358	32,900	8.55
4200	18.80	2.472	1.329	0.385	36,100	8.58

$k_3 = 2.14 \pm 0.03 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$

RUN N₁₇

$$(\text{Cr}^{\text{II}})_0 = 6.134 \times 10^{-3} \text{ mole.l}^{-1}$$

Ionic Strength = 0.50

$$(\text{yne})_0 = 1.714 \times 10^{-3} \text{ mole.l}^{-1}$$

Temperature = 40.0°

$$(\text{K}_2\text{Cr}_2\text{O}_7) = 0.4731 \text{ g.l}^{-1}$$

pH = 2.30

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	4k ₃
0	30.64	3.067	1.714	0	0	
60	30.20	3.023	1.670	0.044	2,840	47.4
420	28.50	2.853	1.500	0.214	15,300	36.4
960	26.75	2.678	1.325	0.389	31,600	32.9
1380	25.45	2.548	1.195	0.519	46,700	33.9
1800	24.40	2.442	1.089	0.625	61,700	34.3
2400	23.30	2.332	0.979	0.735	80,400	33.5
3000	22.40	2.242	0.889	0.825	98,800	32.9
3600	21.55	2.157	0.804	0.910	119,600	33.2

$$k_3 = 8.36 \pm 0.09 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$$

RUN N₁₈

$(\text{Cr}^{\text{II}})_0 = 5.954 \times 10^{-3} \text{ mole.l}^{-1}$
 $(\text{yne})_0 = 1.714 \times 10^{-3} \text{ mole.l}^{-1}$
 $(\text{K}_2\text{Cr}_2\text{O}_7) = 0.4731 \text{ g.l}^{-1}$

Ionic Strength = 0.50

Temperature = 40.0°

pH = 3.05

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	$4k_3$
0	29.77	2.980	1.714	0	0	
60	29.00	2.993	1.637	0.077	5,920	98.6
420	25.45	2.548	1.282	0.432	39,400	93.8
840	23.05	2.307	1.041	0.673	75,200	89.5
1260	21.65	2.167	0.901	0.813	109,000	86.6
1680	20.50	2.052	0.786	0.928	135,000	80.5
2100	19.70	1.972	0.706	1.008	162,000	77.1

$k_3 = 21.4 \pm 0.9 \text{ l}^2.\text{mole}^{-2}.\text{sec}^{-1}$

RUN N₁₉

$$(\text{Cr}^{\text{II}})_0 = 5.918 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Ionic Strength} = 0.50$$

$$(\text{yne})_0 = 1.714 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Temperature} = 40.0^\circ$$

$$(\text{K}_2\text{Cr}_2\text{O}_7) = 0.4731 \text{ g.l}^{-1}$$

$$\text{pH} = 3.45$$

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	$4k_3$
0	29.57	2.959	1.714	0	0	
55	28.45	2.848	1.603	0.111	7,940	150
420	23.60	2.362	1.117	0.597	65,500	156
780	21.35	2.137	0.892	0.822	107,000	137
1140	19.70	1.972	0.727	0.987	156,000	137
1500	18.65	1.867	0.622	1.092	198,000	132
1860	17.95	1.797	0.552	1.162	234,000	126
2220	16.80	1.682	0.437	1.277	311,000	140

$$k_3 = 34.3 \pm 0.4 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$$

RUN N₂₀

$$(\text{Cr}^{\text{II}})_0 = 5.966 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Ionic Strength} = 0.50$$

$$(\text{yne})_0 = 1.714 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Temperature} = 40.0^\circ$$

$$(\text{K}_2\text{Cr}_2\text{O}_7) = 0.4731 \text{ g.l}^{-1}$$

$$\text{pH} = 4.55$$

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	$4k_3$
0	29.80	2.983	1.714	0	0	
60	27.70	2.773	1.504	0.210	15,800	278
355	22.10	2.212	0.943	0.771	93,800	264
660	19.40	1.942	0.673	1.041	172,000	261
960	17.80	1.782	0.513	1.201	251,000	262
1380	16.05	1.607	0.338	1.376	398,000	288
1800	15.45	1.547	0.278	1.436	477,000	265

$$k_3 = 65.8 \pm 0.9 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$$

RUN T₂

$$(\text{Cr}^{\text{II}})_0 = 6.10 \times 10^{-3} \text{ mole.l}^{-1}$$

Ionic Strength = 0.5

$$(\text{yne})_0 = 6.20 \times 10^{-3}$$

Temperature = 40°

Spectrophotometric Run

pH = 5.65

time (secs)	D - D ₀	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	4k ₃
0	0	3.05	6.20	0	0	
30	0.186	2.42	5.57	0.63	14,400	480
40	0.232	2.26	5.41	0.79	19,900	498
50	0.269	2.14	5.29	0.91	23,600	472
60	0.308	2.00	5.15	1.05	30,800	513
70	0.331	1.92	5.07	1.13	34,900	499
80	0.358	1.83	4.98	1.22	40,000	500
100	0.396	1.70	4.85	1.35	48,400	484
125	0.448	1.52	4.67	1.53	58,000	464
150	0.467	1.45	4.60	1.60	70,000	467
175	0.493	1.37	4.52	1.68	79,000	451
200	0.513	1.30	4.45	1.75	87,000	435
250	0.563	1.13	4.28	1.92	114,000	456
300	0.600	1.01	4.16	2.04	139,000	463
350	0.640	0.87	4.02	2.18	178,000	509

$$k_3 = 120 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$$

RUN S₈

$(Cr^{II})_0 = 2.764 \times 10^{-2} \text{ mole.l}^{-1}$
 $(yne)_0 = 0.884 \times 10^{-2} \text{ mole.l}^{-1}$
 $(K_2Cr_2O_7) = 1.2820 \text{ g.l}^{-1}$

$(AcOH) = 1.6 \text{ mole.l}^{-1}$
 $(H_3O^+) = 0.501 \text{ mole.l}^{-1}$

$\text{Ionic Strength} = 0.50$
 $\text{Temperature} = 40.0^\circ$
 $pH = 0.30$

time (secs)	Titre (ml.)	$10^{-2} \cdot (a-x)$ mole.l ⁻¹	$10^{-2} \cdot (b-x)$ mole.l ⁻¹	$10^{-2} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	$4k_3$
0	41.40	1.382	0.884	0	0	
100	41.30	1.379	0.881	0.003	20	0.200
360	41.05	1.371	0.873	0.011	68	0.189
780	40.65	1.357	0.859	0.025	153	0.196
1320	40.15	1.351	0.843	0.041	260	0.197
1800	39.70	1.326	0.828	0.056	358	0.199
2400	39.10	1.306	0.808	0.076	499	0.208
3120	38.60	1.289	0.791	0.093	631	0.202
3600	38.25	1.277	0.779	0.105	723	0.201
5000	37.15	1.240	0.742	0.142	1031	0.206
7000	36.10	1.205	0.707	0.177	1360	0.194
8500	35.10	1.172	0.674	0.210	1700	0.199

$k_3 = 0.050 \pm 0.001 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$

RUN S₇

$(\text{Cr}^{\text{II}})_0 = 2.760 \times 10^{-2} \text{ mole.l}^{-1}$
 $(\text{yne})_0 = 0.884 \times 10^{-2} \text{ mole.l}^{-1}$
 $(\text{K}_2\text{Cr}_2\text{O}_7) = 1.2820 \text{ g.l}^{-1}$

$(\text{AcOH}) = 1.6 \text{ mole.l}^{-1}$
 $(\text{H}_3\text{O}^+) = 0.316 \text{ mole.l}^{-1}$

$\text{Ionic Strength} = 0.50$
 $\text{Temperature} = 40.0^\circ$
 $\text{pH} = 0.50$

time (secs)	Titre (ml.)	$10^{-2} \cdot (a-x)$ mole.l ⁻¹	$10^{-2} \cdot (b-x)$ mole.l ⁻¹	$10^{-2} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	$4k_3$
0	41.33	1.380	0.884	0	0	
50	41.25	1.377	0.881	0.003	17	0.344
300	40.75	1.361	0.865	0.019	117	0.390
700	40.05	1.337	0.841	0.043	271	0.387
1080	39.40	1.316	0.820	0.064	416	0.385
1500	38.75	1.294	0.798	0.086	576	0.384
2000	38.00	1.269	0.773	0.111	768	0.384
2600	37.15	1.240	0.744	0.140	1018	0.392
3600	36.00	1.202	0.706	0.178	1370	0.380
4800	34.65	1.157	0.661	0.223	1840	0.383
8000	31.80	1.061	0.565	0.319	3120	0.390
22,400	29.75	0.993	0.438	0.447	8690	0.388

$k_3 = 0.965 \pm 0.008 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$

RUN S₉

$$(\text{Cr}^{\text{II}})_0 = 2.756 \times 10^{-2} \text{ mole.l}^{-1}$$

$$\text{Ionic Strength} = 0.50$$

$$(\text{yne})_0 = 0.884 \times 10^{-2} \text{ mole.l}^{-1}$$

$$\text{Temperature} = 40.0^\circ$$

$$(\text{K}_2\text{Cr}_2\text{O}_7) = 1.2820 \text{ g.l}^{-1}$$

$$(\text{AcOH}) = 1.6 \text{ mole.l}^{-1}$$

$$\text{pH} = 0.10$$

time (secs)	Titer (ml.)	$10^{-2} \cdot (a-x)$ mole.l ⁻¹	$10^{-2} \cdot (b-x)$ mole.l ⁻¹	$10^{-2} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	$4k_3$
0	41.27	1.378	0.884	0	0	
70	40.75	1.361	0.867	0.017	102	1.46
360	38.70	1.292	0.798	0.086	575	1.60
780	36.55	1.220	0.726	0.158	1180	1.51
1200	34.40	1.149	0.655	0.229	1910	1.59
1800	32.45	1.084	0.590	0.294	2760	1.53
2400	30.55	1.020	0.526	0.358	3790	1.57
3240	28.85	0.963	0.469	0.415	4970	1.53
4200	27.15	0.907	0.413	0.471	6420	1.53

$$k_3 = 0.385 \pm 0.005 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$$

RUN S₅

$$(\text{Cr}^{\text{II}})_0 = 1.046 \times 10^{-2} \text{ mole.l}^{-1}$$

$$\text{Ionic Strength} = 0.50$$

$$(\text{yne})_0 = 3.930 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Temperature} = 40.0^\circ$$

$$(\text{K}_2\text{Cr}_2\text{O}_7) = 0.6410 \text{ g.l}^{-1}$$

$$(\text{AcOH}) = 1.6 \text{ mole.l}^{-1}$$

$$\text{pH} = 2.10$$

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\frac{dx}{(a-x)^2(b-x)}$	$4k_3$
0	31.32	5.231	3.930	0	0	
90	29.95	5.002	3.701	0.229	2,300	25.6
600	24.80	4.142	2.841	1.089	15,200	25.3
1500	19.85	3.315	2.014	1.916	40,500	27.0
2400	17.40	2.906	1.605	2.325	64,200	26.7
3600	15.65	2.614	1.313	2.617	90,700	25.2
5400	13.80	2.305	1.004	2.926	136,000	25.2
8400	12.10	2.021	0.720	3.210	208,000	24.8

$$k_3 = 6.31 \pm 0.06 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$$

RUN K₁₁

$$(\text{Cr}^{\text{II}})_0 = 9.830 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Ionic Strength} = 0.50$$

$$(\text{yne})_0 = 1.750 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Temperature} = 40.0^\circ$$

$$(\text{K}_2\text{Cr}_2\text{O}_7) = 0.4720 \text{ g.l}^{-1}$$

$$(\text{AcOH}) = 1.6 \text{ mole.l}^{-1}$$

$$\text{pH} = 2.85$$

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	$4k_3$
0	49.18	4.915	1.750	0	0	
90	47.55	4.751	1.586	0.164	4,170	46.3
340	42.95	4.292	1.130	0.623	20,700	60.7
660	39.45	3.942	0.777	0.973	42,700	64.8
980	37.05	3.702	0.537	1.213	66,300	67.7
1300	35.55	3.552	0.387	1.363	91,200	70.2
1620	34.60	3.456	0.291	1.459	113,000	69.8
2000	33.60	3.356	0.191	1.559	146,000	76.1
2500	32.75	3.272	0.107	1.643	191,000	73.1

$$k_3 = 17.5 \pm 1.3 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$$

RUN L₂

$$(\text{Cr}^{\text{II}})_0 = 6.162 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Ionic Strength} = 0.50$$

$$(\text{yne})_0 = 1.642 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Temperature} = 40.0^\circ$$

$$(\text{K}_2\text{Cr}_2\text{O}_7) = 0.4720 \text{ g.l}^{-1}$$

$$(\text{AcOH}) = 1.6 \text{ mole.l}^{-1}$$

$$\text{pH} = 4.30$$

time (secs)	Titre (ml.)	$10^{-3}(a-x)$ mole.l ⁻¹	$10^{-3}(b-x)$ mole.l ⁻¹	$10^{-3}x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	$4k_3$
0	30.83	3.081	1.642	0	0	
90	30.60	3.058	1.619	0.023	1,670	18.6
400	30.00	2.998	1.559	0.083	5,660	14.2
800	29.10	2.908	1.469	0.173	12,500	15.6
1200	28.40	2.838	1.399	0.243	18,300	15.3
1600	27.50	2.748	1.309	0.333	27,000	16.9
2000	26.80	2.678	1.239	0.403	34,400	17.2
2400	26.30	2.628	1.189	0.453	40,200	16.8

$$k_3 = 4.20 \pm 0.07 \text{ l}^2.\text{mole}^{-2}.\text{sec}^{-1}$$

RUN K₂

$$(\text{Cr}^{\text{II}})_0 = 7.758 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Ionic Strength} = 0.50$$

$$(\text{yne})_0 = 1.750 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Temperature} = 30.0^\circ$$

$$(\text{K}_2\text{Cr}_2\text{O}_7) = 0.4243 \text{ g.l}^{-1}$$

$$(\text{AcOH}) = 1.6 \text{ mole.l}^{-1}$$

$$\text{pH} = 1.40$$

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	$4k_3$
0	-----	3.879	1.750	0	0	
200	43.10	3.871	1.742	0.008	280	1.4 ₀
600	42.95	3.858	1.729	0.021	880	1.5 ₀
1000	42.10	3.781	1.652	0.098	3,900	3.9 ₀
1400	42.05	3.777	1.648	0.102	4,110	2.94
1800	-----	-----	-----	-----	-----	-----
2200	41.50	3.728	1.599	0.151	6,240	2.84
2600	41.35	3.714	1.585	0.165	6,880	2.65
3000	41.05	3.687	1.558	0.192	8,040	2.68
3400	40.55	3.642	1.513	0.237	10,370	3.05
3800	40.20	3.611	1.482	0.268	11,900	3.13
4200	40.30	3.620	1.491	0.259	11,400	2.72
4600	39.80	3.575	1.446	0.304	13,800	2.99
5000	39.30	3.530	1.401	0.349	16,400	3.28
5400	39.40	3.538	1.401	0.341	15,900	2.95
5800	39.00	3.503	1.374	0.376	17,900	3.09
6200	38.90	3.494	1.365	0.385	18,500	2.99
6600	38.80	3.485	1.356	0.394	19,100	2.90
7000	38.46	3.449	1.320	0.430	21,300	3.04

$$k_3 = 0.758 \pm 0.009 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$$

RUN K₃

(Cr^{II})₀ = 8.006 x 10⁻³ mole.l⁻¹ Ionic Strength = 0.50

(yne)₀ = 1.750 x 10⁻³ mole.l⁻¹ Temperature = 35.0°

(K₂Cr₂O₇) = 0.4243 g.l⁻¹ (A₀OH) = 1.6 mole.l⁻¹ pH = 1.40

time (secs)	Titre (ml.)	10 ⁻³ .(a-x) mole.l ⁻¹	10 ⁻³ .(b-x) mole.l ⁻¹	10 ⁻³ .x mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	4k ₃
0	44.65	4.003	1.750	0	0	
200	44.65	-----	-----	-----		
1000	43.70	3.925	1.672	0.068	2,730	2.73
1800	42.80	3.884	1.591	0.159	6,200	3.44
2200	42.45	3.813	1.560	0.190	7,540	3.43
2600	42.20	3.790	1.537	0.213	8,560	3.29
3000	41.65	3.741	1.488	0.262	10,870	3.62
3400	41.45	3.723	1.470	0.280	11,740	3.45
3800	41.15	3.696	1.443	0.307	13,100	3.44
4200	40.55	3.642	1.389	0.361	15,900	3.79
4600	40.55	3.642	1.389	0.361	15,900	3.46
5400	39.95	3.588	1.335	0.415	18,900	3.51
5800	39.65	3.561	1.308	0.443	20,600	3.54
6200	39.60	3.557	1.304	0.446	20,800	3.35
6600	39.40	3.539	1.286	0.464	21,900	3.32
7000	38.85	3.490	1.237	0.513	25,000	3.58
7800	38.50	3.458	1.205	0.545	27,200	3.49

k₃ = 0.865 ± 0.005 l².mole⁻².sec⁻¹

RUN K₁

$(Cr^{II})_0 = 7.954 \times 10^{-3} \text{ mole.l}^{-1}$

Ionic Strength = 0.50

$(yne)_0 = 1.691 \times 10^{-3} \text{ mole.l}^{-1}$

Temperature = 50.0°

$(K_2Cr_2O_7) = 0.4243 \text{ g.l}^{-1}$

$(AcOH) = 1.6 \text{ mole.l}^{-1}$

pH = 1.40

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	4k ₃
0	44.27	3.977	1.691	0	0	
400	43.55	3.912	1.626	0.065	2,520	6.31
1600	42.05	3.777	1.491	0.200	9,380	5.86
2000	41.65	3.741	1.455	0.236	10,080	5.04
4000	39.65	3.561	1.275	0.416	20,100	5.02
4400	39.35	3.534	1.248	0.443	21,700	4.94
4800	39.15	3.516	1.230	0.461	23,400	4.88
5200	38.65	3.472	1.186	0.505	25,800	4.96
5600	38.25	3.426	1.150	0.541	28,400	5.07
6000	37.90	3.404	1.118	0.573	31,000	5.17
6400	37.55	3.372	1.086	0.605	33,400	5.23
6800	37.40	3.359	1.073	0.618	34,500	5.08
7200	37.25	3.346	1.060	0.631	35,500	4.93
7600	36.90	3.314	1.028	0.663	38,400	5.05

$k_3 = 1.34 \pm 0.04 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$

RUN N₁₁

(Cr^{II})₀ = 6.494 x 10⁻³ mole.l⁻¹

(yne)₀ = 1.539 x 10⁻³ mole.l⁻¹

(K₂Cr₂O₇) = 0.6905 g.l⁻¹

Ionic Strength = 0.50

Temperature = 40.0°

(AcOH) = 1.6 mole.l⁻¹

pH = 1.40

time (secs)	Titre (ml.)	10 ⁻³ .(a-x) mole.l ⁻¹	10 ⁻³ .(b-x) mole.l ⁻¹	10 ⁻³ .x mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	4k ₃
0	22.21	3.247	1.539	0	0	
450	22.00	3.216	1.508	0.031	1,980	4.40
960	21.75	3.180	1.472	0.067	4,330	4.51
1,500	21.50	3.143	1.435	0.104	6,880	4.59
2,000	21.30	3.114	1.406	0.133	8,970	4.49
2,600	21.05	3.078	1.370	0.169	11,700	4.50
3,400	20.75	3.034	1.326	0.213	15,200	4.47
4,000	20.50	2.997	1.289	0.250	118,300	4.58
4,500	20.25	2.961	1.253	0.286	21,500	4.78
5,000	20.15	2.946	1.238	0.301	22,800	4.56
5,800	19.90	2.909	1.201	0.338	26,400	4.56
6,600	19.65	2.873	1.165	0.374	30,000	4.55
7,400	19.45	2.844	1.135	0.403	33,400	4.51
9,600	18.85	2.756	1.048	0.491	43,400	4.52
13,000	18.05	2.639	0.931	0.608	59,700	4.59
19,000	17.00	2.485	0.777	0.762	87,400	4.60
32,000	15.55	2.273	0.565	0.974	144,000	4.50
46,000	14.40	2.105	0.397	1.142	210,000	4.57

k₃ = 1.13 ± 0.02 l².mole⁻².sec⁻¹

RUN N₁₀

$$(\text{Cr}^{\text{II}})_0 = 6.452 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Ionic Strength} = 0.50$$

$$(\text{yne})_0 = 1.071 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Temperature} = 40.0^\circ$$

$$(\text{K}_2\text{Cr}_2\text{O}_7) = 0.6905 \text{ g.l}^{-1}$$

$$(\text{AcOH}) = 1.6 \text{ mole.l}^{-1}$$

$$\text{pH} = 1.40$$

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	$4k_3$
0	22.07	3.206	1.071	0	0	
400	21.95	3.201	1.054	0.017	1,500	3.87
1,000	21.70	3.173	1.018	0.053	4,970	4.97
1,400	21.60	3.158	1.003	0.068	6,450	4.61
1,900	21.45	3.136	0.981	0.090	8,680	4.57
2,600	21.25	3.107	0.952	0.119	11,800	4.54
3,300	21.05	3.078	0.923	0.148	15,000	4.55
3,900	20.90	3.056	0.901	0.170	17,600	4.51
4,700	20.70	3.026	0.871	0.200	21,200	4.51
5,300	20.55	3.004	0.849	0.222	24,000	4.53
6,000	20.40	2.982	0.827	0.244	27,000	4.50
7,300	20.10	2.939	0.784	0.287	33,100	4.53
10,000	19.55	2.858	0.703	0.368	46,100	4.61
15,500	18.70	2.734	0.579	0.452	71,000	4.58
21,000	18.05	2.639	0.484	0.587	95,800	4.56

$$k_3 = 1.13 \pm 0.03 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$$

RUN N₅

$$(\text{Cr}^{\text{II}})_0 = 5.870 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Ionic Strength} = 0.50$$

$$(\text{yne})_0 = 1.990 \times 10^{-3} \text{ mole.l}^{-1}$$

$$\text{Temperature} = 40.0^\circ$$

$$(\text{K}_2\text{Cr}_2\text{O}_7) = 0.6905 \text{ g.l}^{-1}$$

$$(\text{AcOH}) = 1.6 \text{ mole.l}^{-1}$$

$$\text{pH} = 1.40$$

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	$4k_3$
0	20.50	2.935	1.990	0	0	
200	20.40	2.921	1.976	0.014	720	3.60
1,000	20.15	2.885	1.940	0.050	3,020	3.02
1,700	19.90	2.850	1.905	0.085	5,280	3.11
2,800	19.55	2.800	1.855	0.135	8,540	3.05
4,000	19.20	2.748	1.804	0.186	12,100	3.02
4,800	18.95	2.714	1.769	0.221	14,800	3.08
6,500	18.50	2.649	1.704	0.286	20,000	3.08
8,400	18.05	2.585	1.640	0.350	25,700	3.06
10,000	17.65	2.527	1.582	0.408	31,100	3.11
14,000	17.00	2.434	1.489	0.501	43,500	3.11

$$k_3 = 0.765 \pm 0.008 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$$

RUN N₉

$(Cr^{II})_0 = 6.466 \times 10^{-3} \text{ mole.l}^{-1}$
 $(yne)_0 = 1.140 \times 10^{-3} \text{ mole.l}^{-1}$
 $(K_2Cr_2O_7) = 0.6905 \text{ g.l}^{-1}$

$(AcOH) = 1.6 \text{ mole.l}^{-1}$
 $pH = 1.40$

$Ionic \text{ Strength} = 0.50$
 $Temperature = 40.0^{\circ}$

time (secs)	Titre (ml.)	$10^{-3} \cdot (a-x)$ mole.l ⁻¹	$10^{-3} \cdot (b-x)$ mole.l ⁻¹	$10^{-3} \cdot x$ mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	$4k_3$
0	22.11	3.233	1.140	0	0	
400	22.00	3.216	1.123	0.017	1,020	2.55
1,450	21.80	3.187	1.094	0.046	3,990	2.75
2,200	21.65	3.165	1.072	0.068	5,990	2.72
3,000	21.50	3.143	1.050	0.090	8,080	2.69
3,750	21.35	3.121	1.028	0.112	10,200	2.73
4,250	21.25	3.107	1.014	0.126	11,700	2.75
5400	21.05	3.078	0.985	0.155	14,700	2.72
6,000	20.95	3.063	0.970	0.170	16,300	2.72
7,000	20.80	3.041	0.948	0.192	18,800	2.69
12,000	20.05	2.931	0.838	0.302	32,700	2.69
20,000	18.95	2.770	0.677	0.463	59,00	2.95

$k_3 = 0.683 \pm 0.005 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$

RUN P₁

$$(\text{Cr}^{\text{II}})_0 = 1.974 \times 10^{-2} \text{ mole.l}^{-1}$$

$$\text{Ionic Strength} = 0.5$$

$$(\text{yne})_0 = 1.500 \times 10^{-2} \text{ mole.l}^{-1}$$

$$\text{Temperature} = 25^\circ$$

Spectrophotometric run in H₂O

$$\text{pH} = 1.40$$

time (secs)	D - D ₀	10 ⁻² · (a-x) mole.l ⁻¹	10 ⁻² · (b-x) mole.l ⁻¹	10 ⁻² · x mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	4k ₃
0	0	0.987	1.500	0	0	
50	0.018	0.969	1.482	0.018	140	2.80
100	0.039	0.949	1.462	0.038	263	2.63
220	0.081	0.908	1.421	0.079	600	2.73
340	0.120	0.871	1.384	0.116	920	2.71
700	0.213	0.780	1.293	0.207	1940	2.77
1300	0.318	0.677	1.190	0.310	3530	2.72
2900	0.485	0.514	1.027	0.473	7820	2.70
4000	0.553	0.488	0.961	0.539	10,070	2.68
5500	0.623	0.380	0.893	0.607	15,000	2.73

$$k_3 = 0.68 \pm 0.01 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$$

RUN P₂

$$(\text{Cr}^{\text{II}})_0 = 2.060 \times 10^{-2} \text{ mole.l}^{-1}$$

$$\text{Ionic Strength} = 0.5$$

$$(\text{yne})_0 = 1.500 \times 10^{-2} \text{ mole.l}^{-1}$$

$$\text{Temperature} = 25^{\circ}$$

Spectrophotometric run in H₂O

$$\text{pH} = 1.40$$

time (secs)	D - D ₀	10 ⁻² · (a-x) mole.l ⁻¹	10 ⁻² · (b-x) mole.l ⁻¹	10 ⁻² · x mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	4k ₃
0	0	1.030	1.500	0	0	
100	0.041	0.990	1.460	0.040	241	2.41
240	0.086	0.946	1.416	0.084	590	2.46
400	0.139	0.895	1.365	0.135	990	2.48
750	0.221	0.815	1.285	0.215	1840	2.45
1150	0.304	0.734	1.204	0.296	2920	2.54
1800	0.389	0.651	1.121	0.379	4410	2.45
3000	0.503	0.541	1.011	0.489	7380	2.45
4500	0.597	0.449	0.919	0.581	11,300	2.51

$$k_3 = 0.62 \pm 0.01 \text{ l}^2 \cdot \text{mole}^{-2} \cdot \text{sec}^{-1}$$

RUN P₃

$(Cr^{II})_0 = 2.326 \times 10^{-2} \text{ mole.l}^{-1}$

Ionic Strength = 0.5

$(yne)_0 = 1.517 \times 10^{-2} \text{ mole.l}^{-1}$

Temperature = 25°

Spectrophotometric run in D₂O

pH = 1.40

time (secs)	D - D ₀	10 ⁻² .(a-x) mole.l ⁻¹	10 ⁻² .(b-x) mole.l ⁻¹	10 ⁻² .x mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	4k ₃
0	0	1.163	1.517	0	0	
100	0.009	1.154	1.508	0.009	30	0.30
800	0.062	1.102	1.456	0.061	320	0.40
1,300	0.111	1.055	1.409	0.108	520	0.40
3,000	0.206	0.962	1.316	0.201	1250	0.42
4,700	0.281	0.890	1.244	0.273	1890	0.40
7,600	0.381	0.792	1.146	0.371	3040	0.40
12,000	0.481	0.694	1.048	0.694	4700	0.39
17,500	0.581	0.597	0.951	0.566	7000	0.40

$k_3 = 0.10 \pm 0.01 \text{ l}^2.\text{mole}^{-2}.\text{sec}^{-1}$

RUN P₄

$(Cr^{II})_0 = 1.908 \times 10^{-2} \text{ mole.l}^{-1}$
 $(yne)_0 = 1.517 \times 10^{-2} \text{ mole.l}^{-1}$
Spectrophotometric run in D₂O

Ionic Strength = 0.5

Temperature = 25°

pH = 1.40

time (secs)	D - D ₀	10 ⁻² .(a-x) mole.l ⁻¹	10 ⁻² .(b-x) mole.l ⁻¹	10 ⁻² .x mole.l ⁻¹	$\int \frac{dx}{(a-x)^2(b-x)}$	4k ₃
0	0	0.954	1.571	0	0	
1,000	0.056	0.899	1.462	0.055	420	0.42
3,500	0.156	0.802	1.365	0.152	1,370	0.39
7,000	0.256	0.705	1.268	0.249	2,860	0.41
12,000	0.356	0.608	1.171	0.346	4,550	0.38
20,000	0.456	0.510	1.073	0.444	7,400	0.37
30,000	0.556	0.413	0.976	0.541	11,900	0.40
50,000	0.656	0.316	0.879	0.638	20,000	0.40

$k_3 = 0.096 \pm 0.009 \text{ l}^2.\text{mole}^{-2}.\text{sec}^{-1}$



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For Reference

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